Wash 353 354.

PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. XXV. Nos. 350—364.

JANUARY—DECEMBER, 1909.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW
1910.

RICHARD CLAY AND SONS, LIMITED
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR 1909.

£6 to A. J. Allmand: electromotive properties of the oxides of mercury, and the investigation of some organic gaseous equilibria.

£7 to R. Alpern: condensation of glycerol and its chlorohydrins with various amido-acids.

£8 to D. Bain: synthesis of narcotine.

£15 to E. C. C. Baly: ultra-violet absorption spectra of organic compounds (continued).

£10 to G. Barger: adsorption of iodine.

£5 to T. V. Barker: the regular growth of crystals on each other.

£5 to A. Clayton: preparation and constitution of coumarinic acid (continued).

£9 to Miss M. E. Dobson: attempt to synthesise berberine.

£9 to J. C. Duff: condensations of aromatic aldehydes with homophthalic acids.

£5 to J. A. N. Friend: corrosion of iron at various temperatures (continued).

£8 to H. D. Gardner: resolution of *cyclo*butane and *cyclo*pentane dicarboxylic acids into their optically active modifications.

£15 to C. Gilling: hydroaromatic ketones (continued).

£10 to G. S. Hibbert: reduction of hydroxy-*o*-toluic acid.

£10 to H. Hibbert: affinity of organic compounds, and the constitution of ammonium salts.

£10 to A. Holt, jun.: action of the silent electric discharge upon carbon dioxide and oxygen.

£7 to E. Hope: ethyl benzoylacetate.

£8 to E. Hope: condensation products from cotarnine and benzoylcotarnine.

£7 to J. Lister: attempt to synthesise cotarnic acid.

£7 to T. M. Lowry: dynamic isomerism (continued).

£5 to H. McCombie: action of dehydrating agents on cyanohydrins.

£6 to P. May: studies in the diphenyl series.

£10 to A. N. Meldrum: reduction of hydroxy-*m*-toluic acid (continued).

£15 to W. H. Mills: investigation of optically active compounds.

£8 to G. T. Morgan: organic derivatives of antimony and allied elements.

£5 to G. T. Morgan: influence of substitution on the tinctorial properties of azo-dyes and allied colouring matters (continued).

£6 to W. Parry: action of Grignard's reagents on the esters of hydroxy*iso*butyric, diethyloxalic, and benzilic acids.

£10 to A. G. Perkin: constitution of carthamine.

£17 to R. H. Pickard: isomeric menthols (continued).

£15 to R. Robinson: synthesis of papaverine; and investigation of pyranol salts (continued).

£5 to G. Senter: reactivity of halogens in organic compounds.

£15 to J. L. Simonsen: formation and properties of the *cyclo*butane ring. Attempt to synthesise norpinic acid, and the constitution of the aloins (continued).

£15 to Miss I. Smedley: refractive indices of unsaturated compounds (continued).

£10 1. 8. to S. Smiles: quadrivalent sulphur.

£5 to Clarence Smith: constitution of the hydroxyazo-compounds (continued).

£5 to J. A. Smythe: organic polysulphides.

£10 to R. Storey: resolution of methyltetrahydrobenzoic acid into its optically active modifications (continued).

£6 to R. Storey: conversion of cyclic unsymmetrical imides into *n*-substituted derivatives.

£5 2. 7. to J. J. Sudborough: esterification and hydrolysis of esters (continued).

£2 to D. Thomson: condensation of active methyl*cyclo*hexanone-3 with various aldehydes.

£15 to J. F. Thorpe: transformation of aliphatic dinitriles into alicyclic imino-nitriles.

£8 to C. K. Tinkler: action of bases and of potassium cyanide on alkyl and aryl salts of cyclic bases.

£5 to W. E. S. Turner: molecular complexity of amides, amines, and nitriles in the liquid state.

£5 to W. E. S. Turner and C. J. Peddle: the hydroxyl group as a cause of molecular association.

Total amount granted during 1909 = £369. 4. 3.

LIST OF FELLOWS ELECTED DURING 1909.

Name.	Proposed.	Elected.
Adlam, George Henry Joseph	December 17th, 1908.	February 18th.
Aiyer, A. K. Yegna Narayan	June 17th, 1909	December 2nd.
Anklesaria, Jehangir Dhanjishaw	October 21st, 1909	,, ,,
Annett, Harold Edward	May 6th, 1909	June 17th.
Armstrong, James Alexander Hadden	October 21st, 1909	December 2nd.
Arnfield, Harold	May 6th, 1909	June 17th.
Barker, Donald William Elsom	October 21st, 1909	December 2nd.
Baron, Harold	,, ,,	,, ,,
Bennett, Hugh Garner	February 18th, 1909	May 6th.
Best, Stanley Robert	October 21st, 1909	December 2nd.
Blackburn, Albert Riley	March 18th, 1909	May 6th.
Bletcher, Henry Ernest John	,, ,, ,,	,, ,,
Bottomley, Hubert Frederick	October 21st, 1909	December 2nd.
Breakspear, Henry Shaw	,, ,, ,,	,, ,,
Brunskill, Hubert	December 17th, 1908.	February 18th.
Burger, O. K. H.	October 21st, 1909	December 2nd.
Burt, Frank Playfair	February 18th, 1909.	May 6th.
Bury, Frank Ward	October 21st, 1909	December 2nd.
Callister, William Edward	October 21st, 1909	December 2nd.
Campbell, Walter	March 18th, 1909	May 6th.
Carey, William Gordon	October 21st, 1909	December 2nd.
Caulkin, Howard Alfred	February 4th, 1909	May 6th.
Chamblis, Hardee	June 3rd, 1909	December 2nd.
Chand, Lakshami	October 21st, 1909	,, ,,
Chew, John Henry	February 4th, 1909	May 6th.
Clarke, George	,, ,, ,,	,, ,,
Clayton, Arthur	November 19th, 1908.	February 18th.
Cocksedge, Herbert Edwin	December 3rd, 1908.	,, ,,
Coles, Alfred Bertram	January 21st, 1909	,, ,,
Cooke, Reginald Cyril Herbert	February 18th, 1909.	May 6th.
Coope, John Charles Jesser	November 19th, 1908.	February 18th.
Cooper, George Stanley	February 4th, 1909	May 6th.
Couch, Daniel Little	March 18th, 1909	,, ,,
Couzens, Edward Gordon	,, ,, ,,	,, ,,
Creighton, Henry Jermain Maude	February 18th, 1909.	,, ,,
Crewe, Philip Henry	,, ,, ,,	,, ,,
Dawson, James Ferguson	October 21st, 1909	December 2nd.
Dunlop, John Gunning Moore	May 20th, 1909	June 17th.
Dunn, Frederick Percy	December 3rd, 1908.	February 18th.
Dunningham, Alfred Charles	October 21st, 1909	December 2nd.
Dyche-Teague, Francis Clifford	March 18th, 1909	May 6th.
Edgar, Edward Charles	October 21st, 1909	December 2nd.
Edge, Alfred	,, ,, ,,	,, ,,

Name.	Proposed.	Elected.
Edge, John Harold	April 1st, 1909	June 17th.
Edwards, Frederick Watson	October 21st, 1909	December 2nd.
Egerton, Alfred Charles Glyn	May 6th, 1909	June 17th.
Essex, Harry, jun.	,, ,, ,,	,, ,,
Ewins, Arthur James	October 21st, 1909	December 2nd.
Ferraboschi, Frederic	December 3rd, 1908	February 18th.
Flack, Edmund Victor	November 18th, 1909	December 2nd.
Forrester, George Peters	October 21st, 1909	,, ,,
Forshaw, Arthur	November 4th, 1909	,, ,,
Fowler, William	February 4th, 1909	May 6th.
Fox, John Thomas	January 21st, 1909	February 18th.
Francis, Arthur Gordon	November 19th, 1908	,, ,,
Freymuth, William Adolf	October 21st, 1909	December 2nd.
Fürstenhagen, Otto	,, ,, ,,	,, ,,
Furneaux, George Pomeroy	,, ,, ,,	,, ,,
Furnell, John Thomas	January 21st, 1909	February 18th.
Gardiner, Alexander David	November 4th, 1909	December 2nd.
Gardner, Henry Dent, jun.	October 21st, 1909	,, ,,
Gortner, Ross Aiken	November 19th, 1908	February 18th.
Green, John Wilberforce	December 17th, 1908.	,, ,,
Grist, Charles James	March 18th, 1909	May 6th.
Gwyer, Alfred George Cooper	January 21st, 1909	February 18th.
Harding, Victor John	October 21st, 1909	December 2nd.
Hargreaves, Egerton	February 4th, 1909	May 6th.
Harland, Robert Main	January 21st, 1909	February 18th.
Harvey, Arthur John	October 21st, 1909	December 2nd.
Haworth, Walter Norman	December 3rd, 1908	February 18th.
Haws, John Frederick	February 18th, 1909	May 6th.
Hayward, Eric	December 3rd, 1908	February 18th.
Hendry, Robert Douglas	October 21st, 1909	December 2nd.
Hibbert, Harold	April 1st, 1909	June 17th.
Hickinbotham, Reginald Vernon	February 18th, 1909	May 6th.
Higson, Frank	November 19th, 1908	February 18th.
Holmyard, Eric John	,, 4th, 1909	December 2nd.
Hopkinson, Reginald	February 4th, 1909	May 6th.
Hoseason, James Henry	November 19th, 1908	February 18th.
Hough, Ralph	,, ,, ,,	,, ,,
Jackson, Robert Ernest	December 3rd, 1908	February 18th.
Jeffery, John Hugh	,, ,, ,,	,, ,,
Jones, Henry Humphreys	January 21st, 1909	,, ,,
Keeble, Horace	January 21st, 1909	February 18th.
Kirby, Oswald Farquhar	May 20th, 1909	June 17th.
Lakhani, Hassum A.	June 3rd, 1909	June 17th.
Leech, Benjamin	June 17th, 1909	December 2nd.
Leedham, Joseph	January 21st, 1909	February 18th.
Levy, Leonard Angelo	March 18th, 1909	May 6th.
Lewis, William Cudmore McCullagh	October 21st, 1909	December 2nd.
Livsey, Harry	March 4th, 1909	May 6th.
Lundholm, Carl Olof	October 21st, 1909	December 2nd.

Name.	Proposed.	Elected.
McGillvray, John Esson	December 17th, 1908.	February 18th.
Martin, William George	January 21st, 1909 ..	,, ,,
Matchet, Andrew Sneddon	May 6th, 1909.....	June 17th.
May, Percy	November 19th, 1909	February 18th.
May, Roland Josiah	April 1st, 1909	June 17th.
Metzger, Floyd Jay	February 4th, 1909...	May 6th.
Morley, William Norton	December 17th, 1908	February 18th.
Müller, Robert	March 18th, 1909.....	May 6th.
Muller, John	November 18th, 1909.	December 2nd.
Napier, Thomas	April 1st, 1909	June 17th.
Norris, Roland Victor	October 21st, 1909 ...	December 2nd.
Okell, Frederick Leigh	March 18th, 1909	May 6th.
Owen, Robert Cecil	March 4th, 1909	,, ,,
Painter, Frederick Hubert	December 17th, 1908.	February 18th.
Peixoto, Joãs Cornelio Rodrigues	November 18th, 1909	December 2nd.
Pickard, Joseph Allen	December 3rd, 1908..	February 18th.
Picton, Norman	May 6th, 1909.....	June 17th.
Ping, Francis Hugh	November 4th, 1909 .	December 2nd.
Pope, Frank George	November 19th, 1908	February 18th.
Proud, Charles	October 21st, 1909 ...	December 2nd.
Regan, Colston James	December 17th, 1908.	February 18th.
Resker, Herbert Charles	May 6th, 1909	June 17th.
Ritchings, Walter	October 21st, 1909....	December 2nd.
Robinson, Fred.	May 21st, 1909.....	June 17th.
Robinson, Frederic William	June 17th, 1909.....	December 2nd.
Robinson, Robert	January 21st, 1909 ...	February 18th.
Rogers, Herbert	,, ,, ,,	,, ,,
Rudolf, Norman Scott	March 4th, 1909.....	May 6th.
Sabherwal, Pindi Das	October 21st, 1909 ...	December 2nd.
Sageman, Philip John	November 19th, 1908.	February 18th.
Sawbridge, Barth. Frere	May 6th, 1909	June 17th.
Schulten, J. H. Charles	January 21st, 1909 ...	February 18th.
Segaller, David	December 3rd, 1908 ..	,, ,,
Sinha, Manindra	October 21st, 1909 ...	December 2nd.
Smith, Henry Llewellyn	March 4th, 1909	May 6th.
Stanford, Spencer Boyd Cortis-	October 21st, 1909 ...	December 2nd.
Stephenson, Guy	,, ,, ,,	,, ,,
Stevenson, James Thomas	December 17th, 1908.	February 18th.
Stones, George Bertram	October 21st, 1909 ...	December 2nd.
Strachan, James Thallon	,, ,, ,,	,, ,,
Strohmenger, Arthur Percy	March 4th, 1909.....	May 6th.
Taplin, Edward Walter	June 3rd, 1909.....	December 2nd.
Tapp, Charles	November 18th, 1909	,, ,,
Tate, Arthur Edwin	February 18th, 1909 .	May 6th.
Thomas, Oswald John Dalgatty	February 4th, 1909...	,, ,,
Thoms, Hermann	June 17th, 1909.....	December 2nd.
Tilley, Vernon James	February 4th, 1909...	May 6th.
Tingle, Joseph Grantley	October 21st, 1909...	December 2nd.
Tizard, Henry Thomas	,, ,, ,,	,, ,,
Truelove, Charles William	February 4th, 1909...	May 6th.
Turner, Herbert	October 21st, 1909....	December 2nd.

Name.	Proposed.	Elected.
Usher, Francis Lawry	February 18th, 1909.	May 6th.
Van Essen, Everard Cecil	June 17th, 1909.	December 2nd.
Varley, Reginald Wells	December 3rd, 1908.	February 18th.
Waliaschko Nikolai	October 21st, 1909.	December 2nd.
Walker, George Bilderbeck	March 4th, 1909	May 6th.
Warwick, Guy Ransom	January 21st, 1909	February 18th.
Webster, John	March 18th, 1909.	May 6th.
Weizmann, Charles	October 21st, 1909	December 2nd.
West, Percy Charles Henry	January 21st, 1909	February 18th.
Wheeler, Richard Vernon	November 4th, 1909.	December 2nd.
Wild, Thomas Jabez	January 21st, 1909	February 18th.
Williams, Herbert Ernest	October 21st, 1909	December 2nd.
Wills, Harry Sampson	May 6th, 1909	June 17th
Wilson, Robert William	February 4th, 1909	May 6th.
Woods, George James	May 6th, 1909	June 17th.
Wright, Joseph Pretty	November 18th, 1909.	December 2nd.
Young, Roland Francis	October 21st, 1909	December 2nd.

LIST OF FELLOWS DECEASED DURING 1909.

Name.	Elected.	Died.
Bannister, Richard	January 19th, 1871	September 27th, 1909.
Castell-Evans, John	February 18th, 1903	May 13th, 1909.
Cox, Ebenezer John	December 2nd, 1886	February 6th, 1909.
Ekin, Charles	December 1st, 1864	August 4th, 1909.
*Erlenmeyer, Emil	February 1st, 1883	January 22nd, 1909.
Fuller, John	December 2nd, 1886	May 17th, 1908.
Graham, Charles	May 1st, 1862	November 13th, 1909.
Harrison, Hugh Erat	June 21st, 1883	August 12th, 1909.
Hudleston, Wilfrid Hudleston	March 2nd, 1871	January 29th, 1909.
Johnson, Samuel Henry	May 10th, 1866	March 12th, 1909.
Kielty, John Joseph	December 3rd, 1903	June 13th, 1909.
Mond, Ludwig	February 15th, 1872	December 11th, 1909.
Norton, Fletcher	December 18th, 1854	April 12th, 1909.
Perry, George Edward	December 6th, 1888	July 21st, 1909.
Pontifex, Edmund Alfred	December 4th, 1848	October 12th, 1909.
Redwood, Theophilus Horne	March 17th, 1887	March 31st, 1909.
Roberts, William Brittain	February 19th, 1880	July 25th, 1909.
Russell, William James	March 3rd, 1851	November 12th, 1909
Stewart, Walter	June 20th, 1872	February 11th, 1909.
Stocks, Frederic	June 18th, 1874	May 31st, 1909.
Thomas, Charles	December 7th, 1871	September 30th, 1909.
Thomas, Harry Edgecumbe	March 5th, 1874	February 9th, 1909.
*Thomsen, Julius	May 18th, 1876	February 13th, 1909.
Wardle, Sir Thomas	May 20th, 1875	January 3rd, 1909.
Watson, Alexander Forbes	May 4th, 1893	August 4th, 1909.
Wilson, James Henry	May 16th, 1878	June 1st, 1909.

* Honorary and Foreign Member.

TITLES OF PAPERS COMMUNICATED TO THE SOCIETY DURING 1909.

	Page in Proceedings.	Page in Transactions.
January 21st.		
1. Organic derivatives of silicon. Part IX. Experiments on the resolution of *dl*-benzylethylpropyl*iso*butylsilicanesulphonic acid. By Frederic Stanley Kipping and Harold Davies	9	69
2. The crystallisation of externally compensated mixtures. By Frederic Stanley Kipping and William Jackson Pope	9	103
3. Formation of *cyclo*hexanone derivatives from olefinic compounds. By Siegfried Ruhemann	10	109
4. Synthesis of para-urazine from carbamide. By Frederick Daniel Chattaway	10	235
5. Chlorine derivatives of substituted carbamides. By Frederick Daniel Chattaway and Donald Frederick Sandys Wünsch	11	129
6. Chemical examination of Eriodictyon. Part II. By Frank Tutin and Hubert William Bentley Clewer	12	81
7. The hydration of precipitates. By Spencer U. Pickering	12	123
8. Studies of dynamic isomerism. Part VIII. The relationship between absorption spectra and isomeric change. Absorption spectra of halogen, nitro-, and methyl derivatives of camphor. By Thomas Martin Lowry and Cecil Henry Desch	13	807
9. The relationship between the constitution and the absorption spectra of pyridine and various derivatives. By John Edward Purvis	14	294
10. The action of mustard oils on the ethyl esters of malonic and cyanoacetic acids. Part II. By Siegfried Ruhemann	14	117
11. The interaction of hydrogen and chlorine. By David Leonard Chapman and Patrick Sarsfield MacMahon	15	135
12. Nitrogen chloride. By David Leonard Chapman and Leonard Vodden	15	138
13. The atmospheric oxidation of β-methylhydrindone. By Arthur Henry Salway and Frederic Stanley Kipping	16	166
14. A glucoside from Tephrosia purpurea. (Preliminary note.) By George Clarke, jun., and S. C. Banerjee	16	—
15. Note on the constitution of the carboxyl group. By Ida Smedley	16	231
16. The relation between the chemical constitution and optical properties of the aromatic α- and γ-diketones. By Ida Smedley	17	218

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17. The transformation of aliphatic nitriles into alicyclic imino-compounds. (Preliminary note.) By Jocelyn Field Thorpe	17	—
18. Action of alcohols on metallic calcium. By Frederick Mollwo Perkin and Lionel Pratt	18	159
19. The condensation of oxymethylenecamphor with primary and secondary amino-compounds. By William Jackson Pope and John Read	18	171
20. Note on the variation in the catalytic activity of mineral acids with changes in their concentration. By Arthur Lapworth	19	—
21. The condensation of dimethyldihydroresorcin with ethylamine. By Paul Haas	19	421
February 4th.		
22. The mechanism of the reduction of nitroanilines and nitrophenols. By Bernhard Flürscheim	21	—
23. The relation between the strength of acids and bases and the quantitative distribution of affinity in the molecule. By Bernhard Flürscheim	22	718
24. Note on the determination of the rate of chemical change by measurement of the gases evolved. By Francis Edward Everard Lamplough	23	—
25. The triazo-group. Part VII. Interaction of benzhydroximic chloride and sodium azide. By Martin Onslow Forster	25	184
26. The triazo-group. Part VIII. Azoimides of the monobasic aliphatic acids. By Martin Onslow Forster and Robert Müller	26	191
27. Nitro-derivatives of ortho-xylene. By Arthur William Crossley and Nora Renouf	26	202
28. The divergence of the atomic weights of the lighter elements from whole numbers. By Alfred Charles Glyn Egerton	26	238
29. The constituents of the bark of Prunus serotina. Isolation of *l*-mandelonitrile glucoside. By Frederick Belding Power and Charles Watson Moore	27	243
30. Benzyl and ethyl derivatives of silicon tetrachloride. By Geoffrey Martin and Frederic Stanley Kipping	27	302
31. The formation and reactions of imino-compounds. Part VIII. The formation of methyl derivatives of 2-phenyl-1 : 3-naphthylenediamine from the three tolylacetonitriles. By Stanley Robert Best and Jocelyn Field Thorpe	28	261
32. The effect of contiguous unsaturated groups on optical activity. Part I. By Thomas Percy Hilditch	29	331
33. The miscibility of solids. By Ernest Vanstone	30	590
34. Esterification constants of substituted acrylic acids. Part III. By John Joseph Sudborough and James Mylam Gittins	31	315

	Page in Proceedings.	Page in Transactions.
35. Brazilin, hæmatoxylin, and their derivatives. Part X. The constitution of trimethylbrazilone, of α- and β-anhydrotrimethylbrazilone, and of the corresponding derivatives of hæmatoxylin. By William Henry Perkin, jun., and Robert Robinson	31	381
36. The preparation of disulphides. Part III. The nitrobenzyl disulphides. (A correction.) By Thomas Slater Price and Douglas Frank Twiss	32	—
37. Derivatives of naphthacenequinone. Part III. By Dorothy Harrop, Roland Victor Norris, and Charles Weizmann	33	279
38. The nature of ammoniacal copper solutions. Part II. The solubility of cupric hydroxide in ammoniacal sulphate solutions. By Harry Medforth Dawson	33	370
39. The action of β-rays on photosensitive solutions. By Otto Flaschner	34	327
40. The rusting of iron. By Gerald Tattersall Moody	34	—
41. The iodobenzenemonosulphonic acids. Part I. By Mary Boyle	35	1683
42. Contributions to the chemistry of the terpenes. Part IV. The oxidation of pinene with mercuric acetate. By George Gerald Henderson and James Watson Agnew	35	289
43. Formation of heterocyclic compounds. Part I. 1-Phenylpyrrolidine-2 : 5-dicarboxylic acid from adipic acid. By Henry Rondel Le Sueur	36	273
44. The influence of solvents on the rotation of optically active compounds. Part XIV. Ethyl tartrate in benzaldehyde and in quinoline. By Thomas Stewart Patterson and David Paterson McDonald	36	321
February 18th.		
45. A study of some asymmetric compounds. By Frederic Stanley Kipping	55	408
46. The decomposition and sublimation of ammonium nitrite. By Prafulla Chandra Rây	56	345
47. The estimation of hydroxyl derivatives in mixtures of organic compounds. By Harold Hibbert	57	—
48. A simple method for determining the chemical affinity of organic substances. By Harold Hibbert	57	—
49. Chlorine generated by potassium permanganate: its preparation and purity. By Edgar Wedekind and Samuel Judd Lewis	59	—
50. The isolation of the aromatic sulphinic acids. By John Thomas	60	342
51. Analytical investigation of zirconium metal. By Edgar Wedekind and Samuel Judd Lewis	60	456
52. The action of ethylene dibromide on monomethylaniline. By John Gunning Moore Dunlop and Humphrey Owen Jones	61	416

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53. Salicylidene-*m*-toluidine, a new phototropic compound: salicylideneamines: salicylamides. By Alfred Senier and Frederick George Shepheard	61	441
54. The action of ethyl carbamate on esters of organic acids and mustard oils. By Siegfried Ruhemann and John Gillies Priestley	62	449
55. The hydrolysis of amygdalin by emulsin. Part III. Synthesis of *d*-benzaldehydecyanohydrin. By Samuel James Manson Auld	62	927
March 4th.		
56. The action of fuming sulphuric acid on triphenylsilicol. By Geoffrey Martin and Frederic Stanley Kipping	66	489
57. The ignition-temperatures of gases. By Harold Baily Dixon and Hubert Frank Coward	67	514
58. The alkaloids of Senecio latifolius. By Henry Edgar Watt	68	466
59. An interpretation of the Hantzsch-Werner hypothesis. By Martin Onslow Forster and Frederick Percy Dunn	68	425
60. The triazo-group. Part IX. Transformation of cinnamoylazoimide into cinnamenylcarbimide (cinnamenyl *iso*cyanate). By Martin Onslow Forster	69	433
61. Experiments on the Walden inversion. Part II. The interconversion of the optically active mandelic acids. By Alex. McKenzie and George William Clough	70	777
62. Diazohydroxylamino-compounds and the influence of substituting groups on the stability of their molecules. By Norman Leslie Gebhard and Herbert Bryan Thompson	70	767
63. Tetraketopiperazine. Part II. By Alfred Theophilus de Mouilpied and Alexander Rule	71	549
64. The miscibility of the pyridine bases with water and the influence of a critical-solution point on the shape of the melting-point curve. By Otto Flaschner	71	668
65. The preparation of dichlorocarbamide. By Frederick Daniel Chattaway	72	464
66. Thiotetrahydroquinazolines, methylenecarbamides, dicarbanilinomethylenediamines, and their homologues. By Alfred Senier and Frederick George Shepheard	72	494
67. The distillation of butter-fat, cocoanut oil, and their fatty acids. By Kenneth Somerville Caldwell and William Holdsworth Hurtley	73	853
68. Note on the detection of white or ordinary phosphorus in the igniting composition of lucifer matches. By Thomas Edward Thorpe	73	440
69. Intramolecular rearrangement of the diphenylamine sulphoxides. (Preliminary note.) By Edward de Barry Barnett and Samuel Smiles	74	—

	Page in Proceedings.	Page in Transactions.
70. A crystalline bleaching powder. By Kennedy Joseph Previté Orton and William Jacob Jones	74	751
71. The action of carbon dioxide on nitrites. By Ernest Robert Marle	74	—
72. Estimation of primary, secondary, and tertiary amines. Part I. By John Joseph Sudborough and Harold Hibbert	75	477
73. The condensation of ketones and aldehydes with the sodium derivative of ethyl cyanoacetate. By Walter Norman Haworth	76	480
74. Experiments on the constitution of the aloins. Part I. (Preliminary note.) By Robert Robinson and John Lionel Simonsen	76	—
75. The constituents of Canadian hemp. Part II. Cynotoxin. (Preliminary note.) By Horace Finnemore	77	—
March 18th.		
76. Liquid and solid radium emanation. By Robert Whytlaw Gray and Sir William Ramsay, K.C.B.	82	—
77. Optically active substances which contain no asymmetric atom." (Preliminary note.) By William Henry Perkin, William Jackson Pope, and Otto Wallach	83	—
78. The constituents of the rhizome of Apocynum androsæmifolium. By Charles Watson Moore	85	734
79. The action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part IV. Derivatives of dihydroxyphenyl-acetic, -glycollic, and -glyoxylic acids. By George Barger and Arthur James Ewins	86	552
80. Studies in the azine series. Part I. The constitution of safranine. By John Theodore Hewitt, Sidney Herbert Newman, and Thomas Field Winmill	86	577
81. The condensation of amides with esters of acetylenic acids. By Siegfried Ruhemann	87	984
82. Studies in asymmetric synthesis. Part VII. The influence of the *d*-amyl group. By Alex. McKenzie and Hermann August Müller	88	544
83. Contributions to the chemistry of cholesterol and coprosterol. By Charles Dorée	88	638
84. Iodine dioxide. By Matthew Moncrieff Pattison Muir	88	656
85. A polarimetric method of identifying chitin. By James Colquhoun Irvine	89	564
86. The conversion *d*-α-methyl*iso*serine into *d*-α-methylglyceric acid. By Francis William Kay	90	560
87. The action of steam on iron. (Preliminary note.) By John Albert Newton Friend	90	—
88. The constitution of sulphurous, sulphuric, carbonic, and formic acids. By John Albert Newton Friend	91	—
89. The formation and reactions of imino-compounds. Part IX. The formation of derivatives of *cyclo*pentane from αδ-dicyano-derivatives of butane. By Stanley Robert Best and Jocelyn Field Thorpe	92	685

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6. Books are issued either to the Fellow desiring the loan, or to a person bringing a written order from him. In either case a receipt must be given on the form provided. When a Fellow desires a book or books to be sent to him, he must send to the Librarian a written order, and pay the whole cost of carriage. All books borrowed by Fellows shall be at the risk of the borrower from the moment they are issued or despatched by the Librarian, and until they are returned to him.

7. Books may not be sent out of the United Kingdom.

8. Books which have been bespoken shall circulate in the order of application.

9. Fellows shall be at liberty to retain a book one calendar month, unless, at the expiration of a fortnight, notice is received that the book is required by another Fellow, in which case it must be returned at once. Single parts of journals may not be retained longer than one week.

10. The names of Fellows borrowing books shall be entered by the Librarian, or Officer in attendance, in a book kept for that purpose. When a Fellow returns a book, his voucher shall be given to him, and a record of the return duly made.

11. In the case of Fellows returning books by messenger or public conveyance, the voucher shall be returned by the Librarian through the post.

12. Fellows retaining books longer than the time specified, or neglecting to return them when demanded, shall forfeit the right to borrow books from the Library until the volume or volumes be returned.

13. Fellows to whom books have been issued shall be held responsible for their preservation from injury; and if any book when returned is found to have been damaged, the Council may order that it be repaired or replaced at the expense of the borrower. In the event of any book being lost, or being detained after application has been made for its return, the Council may replace, at the cost of the borrower, the volume or volumes so lost or detained. This rule shall also apply to single parts of current periodicals.

14. For the purpose of revision and cleaning, the Library shall be closed for a fortnight in August of each year; before which time all books must be returned, unless special permission has been previously obtained from the Librarian. In the event of any book not being returned on such occasion, the Council may replace it at the cost of the borrower.

15. No persons other than Fellows of the Society have the privilege of using the Library, except upon a written introduction from a Fellow, with whom rests the responsibility for all books consulted by the person introduced. Such introduction shall be valid for one occasion only.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 350.

Thursday, January 21st, 1909, at 8.30 p.m., SIR WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The minutes of the previous meeting having been read and confirmed, Dr. DIVERS made the following inquiries. Whether one of the objects of the resolution adopted by the Council "to remove some of the disabilities experienced by women chemists" were not, as it appeared to be, to let duly qualified women be "accepted" to enjoy privileges in the Society which men, similarly qualified, were not to be permitted to enjoy on the same terms, and, that being so, whether that object were a just and lawful one? Whether the Council, in taking upon itself to "enact a regulation" (Charter, p. 6) indistinguishable in form and substance from a bye-law, had avoided exceeding its powers merely by not proceeding to call the regulation a bye-law? In what did the resolution concerning Subscribers of the Society differ from the existing bye-law for Associates, except in that an Associate must have passed a ballot of the Fellows? Was it not clear from the Charter that any action by the Council on the resolution would be invalid until the vote of a General Meeting should have made the resolution into a bye-law? Whether the Council must not be exceeding its powers in legislating for women in any way whatever, if it were indeed the case that it would be going beyond its powers were it to accept women as candidates for the Fellowship, they being, it was said, outside the consideration of the Charter? Would not even a General Meeting be exceeding its much greater powers

were it to attempt to frame quasi-bye-laws for those to whom the Charter did not apply? Did the Council in its words "disabilities experienced by women" refer to its assumption that the Charter really imposed upon it disability to receive the candidature of women for the Fellowship? If so, did it need to be pointed out that disabilities, like any other ordinances, were not "experienced" by anyone, but were imposed, and that a Charter did not attempt to limit the powers of any man or woman who was not enjoying the privileges which it bestowed? In speaking of "removing disabilities" did the Council maintain that it could itself escape from or could relieve others of a disability laid upon it or upon them by the Charter? Lastly, was it to be understood that the Council believed, what its words implied, that it would be removing disabilities by granting privileges, supposing that it really could do either of these things?

Messrs. N. C. Akers, J. Brown, R. F. Easton, C. Everitt, A. F. Girvan, C. L. Norman, G. E. Pearson, W. B. Shaw, W. G. Winterson, and F. P. Worley were formally admitted Fellows of the Society.

The PRESIDENT announced a proposal by the Institution of Gas Engineers to perpetuate the memory of the late Sir George Livesey by establishing a Livesey Professorship in Gas Engineering and Fuel at the Leeds University; contributions to the Fund should be addressed to the Secretary of the Institution of Gas Engineers, 39, Victoria Street, Westminster.

Certificates were read for the first time in favour of Messrs.:

Alfred Bertram Coles, M.A., 42, Broadwater Road, Tottenham, N.
John Thomas Fox, Glen Burn, Stollard Street, Clay Cross, near Chesterfield.
John Thomas Furnell, 32, Grosvenor Park Road, Walthamstow.
Alfred George Cooper Gwyer, Ph.D., B.Sc., Keate House, Durdham Down, Bristol.
Robert Main Harland, 296, Willesden Lane, Willesden Green, N.W.
Henry Humphreys Jones, 18, Colquitt Street, Liverpool.
Horace Keeble, Wereham, Stoke Ferry, Norfolk.
Joseph Leedham, 176, Bromford Lane, West Bromwich.
William George Martin, B.Sc., Royal School, Armagh.
Robert Robinson, M.Sc., Field House, Chesterfield.
Herbert Rogers, Stenning House, Cobwell Road, Retford, Notts.
J. H. Charles Schulten, Ph.D., 4, Pollock Street, Calcutta.

Guy Ransom Warwick, B.A., 5 and 6, Fowkes Buildings, Great Tower Street, E.C.

Percy Charles Henry West, 40, The Green, Norton, Co. Durham.

Thomas Jabez Wild, Scott's Laboratories, Southall, Middlesex.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society :

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE,
STRAND, LONDON, W.C.
29th October, 1908.

GENTLEMEN,

I beg to forward you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1909, to which I have affixed, as desired by them, the signatures of Professors Ostwald and Urbain.

The general revision of the values of the atomic weights of the elements, based on the fundamental values for hydrogen, nitrogen, the halogens, silver, etc., as ascertained by the laborious and accurate determinations which have been made in various laboratories during recent years, and to which reference was made in preceding Reports, has now been completed and the Table submitted with the present Report embodies the results of the re-calculations. A number of atomic weights are shown to be slightly influenced by the adoption of the new values, but the changes thus introduced are, it must be admitted, less profound than was generally anticipated. Certain of the values still remain affected by errors far larger than those introduced by the selection of a particular fundamental value of the element with which comparison is made.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee on Atomic Weights, 1909.

Since the publication of our last Report, several important memoirs upon atomic weights have appeared containing data of fundamental significance. They may be summarised as follows :

Hydrogen.—W. A. Noyes (*J. Amer. Chem. Soc.*, 1907, **29**, 1718)

has made complete syntheses of water in five series of determinations. The first series, however, was defective, and is therefore not published by the author. In mean, the four successful series give H = 1·00787, as compared with Morley's figure, 1·00762. The general mean of these values, combined with all other trustworthy determinations, is 1·00779. The rounded-off value, 1·008, is therefore retained in the table.

Chlorine.—Noyes and Weber (*J. Amer. Chem. Soc.*, 1908, **30**, 13) have effected the synthesis of hydrochloric acid, weighing the hydrogen in palladium, the chlorine in potassium chloroplatinate, and also the hydrochloric acid produced by the union of the two elements. From the ratio H : Cl, Cl = 35·458, when H = 1·00779. From the ratio H : HCl, Cl = 35·457.

The same ratios have also been measured by Edgar (*Proc. Roy. Soc.*, 1908, **81**, *A*, 216), but by a different method. The hydrogen, as in former determinations, was weighed in palladium, but the chlorine was prepared by the electrolysis of fused silver chloride, and weighed in the liquid form. The hydrogen chloride was weighed directly in three experiments, and in two others after absorption in water. From the ratio H : Cl, Cl = 35·468. From the ratio H : HCl, Cl = 35·467. With Morley's value for H, the results are nearer Cl = 35·46. Taking all the data together, the value Cl = 35·46 seems to be as near the truth as can be positively asserted now. This includes the former work of Dixon and Edgar, and the density determinations by Guye and Gazarian.

*Sulphur.**—From eighteen determinations of the density of hydrogen sulphide, Baume and Perrot deduce the value S = 32·070. In an earlier investigation by Baume,† who determined the density of sulphur dioxide, he found lower values for S. The figure 32·07, however, is in close agreement with the value obtained by Richards and Jones, when Ag = 107·88, and is doubtless very nearly true.

Lead.—Atomic weight determined by Baxter and Wilson (*Proc. Amer. Acad.*, **43**, 365) from analyses of the chloride. With Ag = 107·93, Pb = 207·19. With Ag = 107·88, Pb = 207·10. This value is still much higher than that previously accepted.

Cadmium.—Blum (*Thesis*, University of Pennsylvania, 1908) has attempted to determine the atomic weight of cadmium by conversion of the oxide into the sulphide. The values obtained range from 112·50 to 112·88, and are admittedly of slight significance.

Tellurium.—In an elaborate memoir upon the atomic weight of tellurium, Baker and Bennett (Trans., 1907, **91**, 1849) give determina-

* Private communication from Prof. P. A. Guye.

† *J. Chim. Phys.*, 1908, **6**, 1. Baume also determined the densities of methyl oxide and methyl chloride.

tions by two new methods. By heating tellurium dioxide with sulphur in such a way that only sulphur dioxide could escape, the ratio TeO_2 to SO_2 was determined. From the mean of twenty-five determinations, Te = 127·609. By direct conversion of tellurium into the tetrabromide, the mean of eighteen determinations was Te = 127·601, when Br = 79·96. Referred to Br = 79·92, this becomes 127 = 54. Several analyses of tellurium tetrachloride, for which the details are not published, gave values for Te between 127·58 and 127·64. On the basis of the modern values for Ag, Cl, and Br, and with due regard to the earlier work of Pellini, Gutbier, Koethner, Norris, Scott, Staudenmaier, and others, the rounded-off figure, Te = 127·5, seems to be fairly acceptable.

Marckwald,* however, by careful dehydration of telluric acid, found values for Te ranging from 126·65 to 126·94. Six experiments were made, the mean of five, rejecting the lowest of all, being Te = 126·85. This falls below the atomic weight of iodine, and is therefore in harmony with the periodic classification. In view of the general agreement between other investigators in favour of a higher figure, Marckwald's work cannot be accepted without confirmation. The controversy over tellurium is evidently not ended.

Rhodium.—Huttlinger (*Diss.*, Erlangen, 1907), working in Gutbier's laboratory, made three reductions in hydrogen of rhodium pentamine chloride. His results, which seem to be preliminary in character, are practically identical with those obtained by Seubert and Kobbe, whose value for rhodium has been accepted since 1890. No change in this atomic weight is needed.

Palladium.—Woernle (*Sitzungsber. phys. med. Soz. Erlangen*, **38**, 296) made seven analyses of palladosamine chloride: two by reductions in hydrogen, three electrolytically. The mean value obtained was Pd = 106·708, presumably computed with the old figures for N and Cl.

Haas (*Diss.*, Erlangen, 1908), from similar reductions of palladosamine bromide, found Pd = 106·75, calculated with N = 14·037 and Br = 79·953. These determinations, like those of Krell, were made under the direction of Professor Gutbier. The results obtained by Krell, Woernle, and Haas agree well together, and also with Amberg's determinations, and are probably quite accurate. Recomputed, with modern values for N and Cl, Pd = 106·7 very nearly, with an uncertainty of not over 0·05.

Lower values were found by Kemmerer (*Thesis*, University of Pennsylvania, 1908), working under Professor Edgar F. Smith. By reduction in hydrogen, palladosamine chloride gave Pd = 106·399 and

* *Ber.*, 1907, **40**, 4730. For a criticism of Marckwald, see Baker, *Chem. News*, 1908, **97**, 209.

106·442 as the means of two series of observations. From palladosamine cyanide the value Pd = 106·458 was obtained. The mean of fifteen determinations, taken as one series, gave Pd = 106·434. The more concordant values cited above seem to be more trustworthy, at least so far as present evidence permits us to judge. Kemmerer's computations were made with N = 14·01 and Cl = 35·473.

Europium.—From analyses of the octahydrated sulphate, Jantsch (*Compt. rend.*, 1908, **146**, 473) finds Eu = 152·03, when S = 32·06 and H = 1·008. The round number 152 is retained in the table. This is probably the nearest significant figure.

Erbium.—By repeated fractionation of erbium compounds, Hofmann and Burger (*Ber.*, 1908, **41**, 308) have isolated an oxide of slightly higher molecular weight than that of the old erbia. To the new metal thus indicated they assign the name "neo-erbium," and by synthesis of the sulphate they find its probable atomic weight to be 167·43. The rounded-off figure 167·4 is given provisionally in the table, to stand until more complete data have been obtained.

Ytterbium.—That the old ytterbium is a mixture of two elements has been proved by Urbain (*Compt. rend.*, 1907, **145**, 759, November 4, 1907. See also *Compt. rend.*, 1908, **146**, 406, and *Chem. Zeit.*, 1908, **32**, 730), in Paris, and Auer von Welsbach,* in Vienna, working almost simultaneously and independently. In his earlier paper, Urbain names the two elements "neoytterbium" and "lutecium," with approximate atomic weights of 170 and 174 respectively. In his second memoir, Urbain gives atomic weights for a series of ytterbium fractionations, ranging from 170·6 to 174·02. Welsbach, whose work appeared later than Urbain's, names the two elements "aldebaranium," atomic weight 172·90, and "cassiopeium," atomic weight 174·23. Since Urbain has clear priority, his nomenclature should be preferred, but the atomic weights need to be more sharply determined. Incidentally, Urbain notes that the atomic weight of thulium is lower than 168·5.

Columbium.—A concordant series of determinations made under the direction of Edgar F. Smith † give columbium an atomic weight of 93·5. This is lower than the value hitherto accepted.

Radium.—Thorpe (*Proc. Roy. Soc.*, 1908, **80**, *A*, 298) has redetermined the atomic weight of radium by analyses of the chloride. In mean his determinations, calculated with Ag = 107·88 and Cl = 35·46, give Ra = 226·64. Thorpe, however, gives preference to the determinations by Mme. Curie, who worked with larger quantities of material, regarding his own work as confirmatory. The recalculated value is 226·4.

* *Monatsh.*, **29**, 181, Feb., 1908. Read before the Vienna Academy, Dec. 19, 1907. † Private communication. The details are shortly to be published.

In their Report for 1908 this Committee recognised the fact that a general revision of the atomic weight table was desirable, and such a revision has now been made. Modern investigations have shown that the fundamental values required modification, and through them many other atomic weights are affected, although the changes thus brought about are less important than they were generally supposed to be. Many atomic weights remain practically unaltered, and in few instances are the changes large, as a comparison of the new table with its predecessors will show. A careful scrutiny of all the evidence was, however, none the less necessary, and the table now offered gives the results thus obtained.

The fundamental atomic weights, the standards of reference employed in the calculations, are as follows; when O = 16.

H, 1·008.	Br, 79·916.
C, 12·00	Ag, 107·880.
N, 14·007.	K, 39·095.
Cl, 35·460.	S, 32·070.

The value for silver is possibly a trifle too low, by from three to five units in the third decimal place. A combination of the best measurements gives Ag = 107·883. In this case, and in others as well, the second place of decimals is given in the table, the third place being uncertain. Thus we have K, 39·10, N, 14·01, Br, 79·92, etc. Only with hydrogen is the third place retained.

In adjusting the other atomic weights, the determinations by Richards * and his colleagues have generally been given preference. They are certainly entitled to the highest weight, but probably not to exclusive consideration. The work of Guye and his associates at Geneva, and the recent direct measurements of the chlorine-hydrogen ratio are also of very great importance. It is to work of this order that we must look for ultimate precision. Important investigations upon atomic weights are now being carried out in several laboratories, and our knowledge of these constants will doubtless become much more exact within the near future.

(Signed) F. W. Clark,
W. Ostwald,
T. E. Thorpe,
G. Urbain.

* An excellent summary of the Harvard work is given by Richards in *J. Chim. Phys.*, 1908, **6**, 92.

1909.

International Atomic Weights.

		O=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	75·0
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·1
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	81·8
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	7·00
Lutecium	Lu	174
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0

		O=16.
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·0
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·62
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·42
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	128
Ytterbium (Neoytterbium)	Yb	172
Yttrium	Y	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

Of the following papers, those marked * were read :

*1. "**Organic derivatives of silicon. Part IX. Experiments on the resolution of *dl*-benzylethylpropyl*iso*butylsilicanesulphonic acid.**" **By Frederic Stanley Kipping and Harold Davies.**

dl-*Benzylethylpropylisobutylsilicane*, $SiEtPr(C_4H_9)\cdot CH_2Ph$, a liquid boiling at 282—283°, has been prepared by treating benzylethylpropylsilicyl chloride (Kipping, *Trans.*, 1907, **91**, 717) with magnesium *iso*butyl bromide; when treated with chlorosulphonic acid, it gives a monosulphonic derivative, which is isolated in the form of its *l*-menthylamine salt.

l-*Menthylamine* dl-*benzylethylpropylisobutylsilicanesulphonate*, $SiEtPr(C_4H_9)\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N,2H_2O$, separates from moist light petroleum in lustrous leaflets, and, when dehydrated, melts at 127—128°; it is very similar in its properties to the corresponding salts of benzylmethylethylpropylsilicanesulphonic acid (*loc. cit.*) and of benzylethyldipropylsilicanesulphonic acid (Marsden and Kipping, *Trans.*, 1908, **93**, 205), although the latter is not a *dl*-compound.

The *strychnine*, *brucine*, *cinchonidine*, *quinine*, and *cinchonine* salts of the *dl*-acid and the corresponding hydrogen alkaloidal salts of the last-named three bases have been prepared; these eight compounds were systematically crystallised under various conditions, but in all cases, except in that of the cinchonine hydrogen salt, the melting or decomposing points and the specific rotations of the extreme fractions of a given salt were identical. The cinchonine hydrogen salt gave fractions having the same decomposing points, but differing widely in specific rotation; whether this difference is due to a resolution of the acid or not is still an open question.

*2. "**The crystallisation of externally compensated mixtures.**" **By Frederic Stanley Kipping and William Jackson Pope.**

The recent publication of Ostromisslensky's paper (*Ber.*, 1908, **41**, 3035) on this subject affords an occasion for briefly recording the results of some work commenced in 1898, but which has not been brought to a definite issue.

On crystallising *dl*-sodium ammonium tartrate (prepared from purified racemic acid) from aqueous solutions of dextrose, and then recrystallising the deposit, the product consisted, in nearly all cases, of the *d*-tartrate, almost or entirely free from the *l*-salt (*Proc.*, 1898, **14**, 113).

It is now shown that similar results are obtained in absence of

dextrose even when the racemic acid, used in the preparation of the sodium ammonium salt, has been repeatedly crystallised from water. This preferential deposition of the *d*-tartrate may be due to the seeding of the solutions by laboratory dust, or to the presence of a minute excess of the *d*-acid in the racemic acid employed; the results obtained on fractionally crystallising commercial racemic acid itself seem to show that the complete removal of extremely small quantities of dextrorotatory impurity is a very difficult matter.

***3. "Formation of *cyclo*hexanone derivatives from olefinic compounds." By Siegfried Ruhemann.**

Although the esters of acetylenic acids form additive products with phenols, olefinic monocarboxylic esters or olefinic monoketones do not unite with sodium phenoxide. Condensation, however, takes place if the number of electronegative groups in an olefinic compound is increased. The additive compound of ethyl benzylideneacetoacetate with sodium phenoxide at once condenses, thus:

$$2CHPh(OPh)\cdot CHAc\cdot CO_2Et = C_{26}H_{28}O_6 + 2C_6H_5\cdot OH,$$

yielding a compound, $C_{26}H_{28}O_6$, which has twice the molecular formula of ethyl benzylideneacetoacetate. The substance is regarded as a *cyclo*hexanone derivative, $CO_2Et\cdot CAc<\begin{matrix}CHPh\cdot CH(CO_2Et)\\ CHPh\text{———}CH_2\end{matrix}>CO$, and this constitution is supported by a number of facts which the closer study of the reaction has furnished.

Similar *cyclo*hexanone derivatives have been obtained by the action of sodium phenoxide on benzylideneacetylacetone, $CHPh{:}CAc_2$, and ethyl ethylideneacetoacetate, $CHMe{:}CAc\cdot CO_2Et$.

On the other hand, but in harmony with the above view of the formation of these *cyclo*hexanone compounds, neither ethyl benzylidenemalonate, $CHPh{:}C(CO_2Et)_2$, nor ethyl benzylidenebenzoylacetate, $CHPh{:}CBz\cdot CO_2Et$, condenses to cyclic compounds, although uniting with sodium phenoxide.

***4. "Synthesis of para-urazine from carbamide." By Frederick Daniel Chattaway.**

By means of dichlorocarbamide, $NHCl\cdot CO\cdot NHCl$, recently described by the author (*Proc. Roy. Soc.*, 1908, **81**, *A*, 381), carbamide can be very simply converted into *p*-urazine, which has hitherto only been obtained by the employment of hydrazine. All that is necessary is to add an aqueous solution of dichlorocarbamide to a strong solution of ammonia, when *p*-urazine, which is very sparingly soluble in water, separates as a white, crystalline precipitate.

In the reaction, one of the chlorine atoms of the dichlorocarbamide is probably replaced by hydrogen, two molecules of the resulting monochlorocarbamide then condensing under the influence of the ammonia, thus:

$$CO\begin{<}{NHH \\ NHCl}+\begin{ClHN \\ HHN}>CO+2NH_3=CO\begin{<}{NH\cdot NH \\ NH\cdot NH}>CO+2NH_4Cl.$$

p-Urazine is readily hydrolysed when heated with concentrated sulphuric acid, carbon dioxide and hydrazine sulphate being produced, thus: $C_2H_4O_2N_4+2H_2O+2H_2SO_4=2CO_2+2NH_2\cdot NH_2,H_2SO_4$. This reaction furnishes a very simple method for the preparation of small quantities of hydrazine.

Discussion.

Dr. Hewitt called attention to the analogy between Dr. Chattaway's process for obtaining hydrazine and the method devised by Raschig, namely, the direct action of hypochlorites on ammonia.

***5. "Chlorine derivatives of substituted carbamides." By Frederick Daniel Chattaway and Donald Frederick Sandys Wünsch.**

The action of chlorine on carbamide should give rise to a monochloro-, a symmetrical and an unsymmetrical dichloro-, a trichloro-, and a tetrachloro-carbamide. Of these, only the *s*-dichloro-derivative has so far been isolated. The action of chlorine on a number of substituted carbamides has been studied, and it has been shown that in such compounds it is possible to replace by chlorine all the hydrogen attached to nitrogen, atom by atom.

Compounds of the types $NHR\cdot CO\cdot NHCl$, $NClR\cdot CO\cdot NHCl$, $NClR\cdot CO\cdot NCl_2$, $NClR\cdot CO\cdot NClR$, and $NR_2\cdot CO\cdot NCl_2$ have been obtained, R being an acyl or an alkyl group.

The monochloroacylcarbamides are beautifully crystalline solids, which are among the most stable of the nitrogen chlorides known. The acyl compounds containing more chlorine, and most of those containing an alkyl group, are liquids which decompose easily on heating.

Nearly all of the possible chlorine derivatives of acetyl-, benzoyl-, methyl-, *s*- and *as*-dimethyl-, ethyl-, *s*-diethyl-, and benzyl-carbamide have been prepared.

It is thus proved that in carbamides the replacement of one hydrogen atom by chlorine does not prevent in any way the replacement of the second hydrogen atom attached to the same nitrogen.

There is every reason, therefore, to believe that the action of

chlorine on carbamide itself gives rise to the other theoretically possible chlorocarbamides, and that these will be obtained when the conditions under which they can exist are ascertained, and when the difficulties attending their isolation have been overcome.

***6. "Chemical examination of Eriodictyon. Part II." By Frank Tutin and Hubert William Bentley Clewer.**

Eriodictyon leaves were shown by Power and Tutin (*Proc. Amer. Pharm. Assoc.*, 1906, **54**, 352) to contain, in addition to other compounds, three new, crystalline substances of a phenolic nature, namely, eriodictyol, $C_{15}H_{12}O_6$ (m. p. 267°), homoeriodictyol, $C_{16}H_{14}O_6$ (m. p. 223°), and a third substance, possessing the formula $C_{16}H_{12}O_6$, which occurred only in very small amount.

The present authors have employed a larger amount of the extract of *eriodictyon* leaves, and, after a prolonged process of separation, have isolated a larger amount of the last-mentioned compound, together with two new substances.

Chrysoeriol, $C_{16}H_{12}O_6$, the substance previously isolated in small amount, forms golden-yellow leaflets, and does not melt at 337°. It contains three hydroxyl groups, and yields *triacetylchrysoeriol*,

$$C_{16}H_9O_6(CO\cdot CH_3)_3,$$

which melts at 211—212°.

Xanthoeridol, $C_{18}H_{14}O_7$, crystallises in yellow needles melting at 258°. *Triacetylxanthoeridol*, $C_{18}H_{11}O_7(CO\cdot CH_3)_3$, melts at 175—176°.

Eriodonol, $C_{19}H_{18}O_7$, separates from dilute alcohol in pale yellow needles, which contain one molecule of water of crystallisation and melt at 199°; the anhydrous substance melts at 209°. It yields a *tetra-acetyl* derivative melting at 131°.

***7. "The hydration of precipitates." By Spencer U. Pickering.**

Many substances which are precipitated from aqueous solution are capable of emulsifying oils, and, by adjusting the amount of oil in the emulsion, the latter may be obtained of the same density as the liquid. By determining the density of this liquid, the density of the oil, and that of the precipitate in the anhydrous conditions, and by ascertaining the weight of oil required to float a given weight of precipitate in two liquids of different densities, the weight of water combined with the anhydrous precipitate may be determined. The precipitate selected was the compound $10CuO,SO_3,CaSO_4,Na_2SO_4$, which is of uniform composition when thrown down by adding lime-water to copper sulphate in the presence of varying quantities of sodium

sulphate. The amount of water combined with it was found to be about $42H_2O$. It was also ascertained that the water possessed the same specific gravity of ice, as in the case of the water of crystallisation of most hydrated salts.

Discussion.

The President called attention to the fact that Dr. Chichester Bell had, more than ten years ago, made experiments on the velocity of sound in melted ice at $+0{\cdot}5°$, and in cooled water at the same temperature. The velocities appeared to differ. Experiments by Dr. Wilsmore, unpublished, on the density of melted ice, and of cooled water, were indecisive, owing to the lapse of time before an accurate density could be determined.

He also reminded Mr. Pickering that Playfair and Joule had concluded from their experiments that "water of crystallisation" has the same molecular volume as ice.

***8. "Studies of dynamic isomerism. Part VIII. The relationship between absorption spectra and isomeric change. Absorption spectra of halogen, nitro-, and methyl derivatives of camphor." By Thomas Martin Lowry and Cecil Henry Desch.**

The band noted by Baly and by Hartley in the ultra-violet absorption spectrum of camphor at a concentration of $N/10$ appears also in the spectrum of β-bromocamphor; in both cases the band is weakened by diluting to $N/100$, but is restored by the addition of alkali. A similar band of rather greater intensity is seen in the spectrum of α-bromocamphor at a concentration of $N/100$; as this band is developed by neutral solutions in which the α-bromo-compound is stable, and is only slightly intensified when a condition of equilibrium between isomerides is set up by the addition of alkali, its appearance cannot well be associated with the occurrence of reversible isomeric change.

No marked change is seen in the absorption spectrum of α-bromocamphor when a halogen is introduced into the β- or π-position, but the band is no longer developed when the second α-hydrogen atom is displaced by a halogen or by a nitro-group; it may therefore be associated with the presence of a displaceable hydrogen atom in the group $-CHX{\cdot}CO-$, although not dependent on any actual transference of the atom; α'-bromo-α-methylcamphor appears, however, to produce a shallow band.

The weak band of nitrocamphor is greatly intensified by alkalis, but does not appear in the spectrum of the anhydride derived from the pseudo-form; it is therefore dependent on the presence of a

displaceable hydrogen atom rather than on the occurrence of a pseudo-nitro-structure. The β- and π-bromo-derivatives behave like nitrocamphor, but the α-halogen derivatives, which do not undergo isomeric change in solution, produce no absorption band. Nitrocamphane does not give rise to a band either alone or in presence of alkali.

9. "The relationship between the constitution and the absorption spectra of pyridine and various derivatives." By John Edward Purvis.

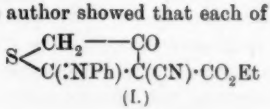
The absorption bands of 3 : 5-dichloropyridine, two isomeric trichloropyridines, two isomeric tetrachloroaminopyridines, α-picoline and several of its derivatives, 2 : 4 : 6-trimethylpyridine and several of its derivatives, and chlorolutidine have been investigated.

The results showed that: (1) the general effect of introducing atoms or groups of atoms into the nucleus is to increase the persistence of the absorption band as well as to shift it towards the red end of the spectrum, whilst when they are introduced into the side-chains they generally decrease the persistence. (2) The weighting of the nucleus does not, however, always mean that the absorption band is shifted towards the red end. The type and the spatial position of the introduced atoms or groups are factors in determining the absorption. (3) In isomeric substances, the spatial positions of the substituting atoms in the nucleus are of considerable importance in influencing the position and the persistence of the absorbed rays. (4) The substitution of atoms in the side-chains does not exert the same marked influence as when they are substituted in the nucleus. (5) The addition of hydrochloric acid to 2 : 4 : 6-trimethylpyridine and α-picoline (as well as to pyridine and lutidine) exerts a marked influence on the vibrations of the nucleus, and the effect is very similar to that produced when chlorine atoms are introduced into the nucleus.

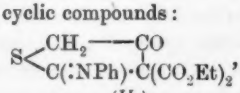
Considerations on the influence of the changing valency of the nitrogen atom and other conditions in explanation of these facts were discussed.

10. "The action of mustard oils on the ethyl esters of malonic and cyanoacetic acids. Part II." By Siegfried Ruhemann.

The author showed that each of the cyclic compounds:



(I.)



(II.)

which he described recently (*Trans.*, 1908, **93**, 621) as existing in two modifications, namely, a yellow and a colourless one, only occur in one form. He was led to this result in the course of a comparative study of these substances, and the similarly constituted compound: $S<^{CH_2\cdot CO}_{CO-NPh}$. Like the latter, the yellow cyclic compound (I) (and also II) condenses with aldehydes with the formation of compounds of the general formula $S<^{C(:CHR)\cdot CO}_{C(:NPh)-C(CN)\cdot CO_2Et}$. It was found that the same products were formed from the colourless compound, and this fact led to the view that both specimens of (I) were identical. The author was able to verify this conclusion.

11. "The interaction of hydrogen and chlorine."
By David Leonard Chapman and Patrick Sarsfield MacMahon.

The authors have shown that the statement of Bunsen and Roscoe, that the rate of photochemical action between chlorine and hydrogen in a mixture containing equivalent amounts of these gases is reduced by the addition of a small volume either of hydrogen or chlorine, cannot be substantiated. Hydrogen and chlorine prepared by the electrolysis of concentrated hydrochloric acid do not possess the alleged inhibitive influence if sufficient precautions are taken to exclude air. It is considered likely that the hydrogen used by Bunsen and Roscoe contained oxygen. This is the more probable, as the gas employed by them was prepared by the electrolysis of dilute sulphuric acid.

12. "Nitrogen chloride."
By David Leonard Chapman and Leonard Vodden.

The authors have shown by a direct analysis that the amount of hydrogen contained in the vapour of nitrogen chloride prepared by the action of chlorine on a neutral solution of ammonium chloride is inappreciable. In harmony with this result, the ratio of nitrogen to chlorine is found to agree very closely with the formula NCl_3. Gattermann's conclusion that the freshly-prepared chloride contains hydrogen which can only be replaced by the continued action of chlorine is therefore called in question.

A method by which the ammonium chloride resulting from the hydrolysis of nitrogen chloride with hydrochloric acid can be isolated without the aid of a reducing agent was described. The method affords the first entirely satisfactory demonstration of the reversibility of the change expressed by the equation:

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

13. "The atmospheric oxidation of β-methylhydrindone."
By Arthur Henry Salway and Frederic Stanley Kipping.

β-Methylhydrindone, $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CHMe$ (Kipping and Clarke, *Trans.*, 1903, **83**, 913), is slowly oxidised on exposure to the air, giving a mixture of compounds from which acetic, phthalic, and benzylmethylketone-*o*-carboxylic acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$, may be isolated; a small amount of a neutral compound, melting at 211°, is also present in the crude oxidation product.

It is suggested that the ketonic form of methylhydrindone (compare Kipping, *Proc.*, 1902, **18**, 34) first undergoes change to the enolic modification, which then combines directly with a molecule of oxygen in much the same way as unsaturated compounds combine with a molecule of ozone; this additive product is then decomposed by water, giving benzylmethylketone-*o*-carboxylic acid, and by similar processes the latter is oxidised to phthalic and acetic acids.

14. "A glucoside from Tephrosia purpurea." (Preliminary note.)
By George Clarke, jun., and S. C. Banerjee.

Tephrosia purpurea, Pers. (nat. ord. *leguminosae*), a small woody annual, grows luxuriantly during the monsoon in many waste tracts of the United Provinces of Agra and Oudh. The leaves yield a crystalline glucoside on extraction with either ethyl alcohol or acetone, and subsequently treating the evaporated extract with water and light petroleum to separate tar. The yield from one extraction is approximately 2 per cent. on the dried leaves. The glucoside melts and decomposes at 180—185° (uncorr.), and on hydrolysis with dilute sulphuric acid yields quercetin and dextrose. It appears, therefore, to be identical with osyritrin (A. G. Perkin, *Trans.*, 1897, **71**, 1134).

15. "Note on the constitution of the carboxyl group."
By Ida Smedley.

From a consideration of the physical and chemical properties of the carboxylic acids, the constitution $\cdot C<\begin{matrix}O\\OH\end{matrix}$ is suggested for the carboxyl group as better representing its physical and chemical behaviour.

16. "The relation between the chemical constitution and optical properties of the aromatic α- and γ-diketones." By Ida Smedley.

Yellow *s*-dibenzoylethylene (m. p. 111°) was prepared by condensing benzoylformaldehyde with acetophenone in the presence of acetic anhydride. This compound is identical with that obtained by Paal and Schulze (*Ber.*, 1900, **33**, 3784) by the action of heat on dibenzoylmalic acid. From a consideration of the solubility, melting point, refractive power, and colour of the *cis*- and *trans*-isomerides, the yellow form, which has the greater solubility, lower melting point, and greater refraction, is regarded as the *cis*-isomeride, and not the *trans*-form as suggested by Paal and Schulze. These two forms furnish the first instance described of a marked difference in the refraction of *cis*- and *trans*-isomerides. The molecular refractions of the following compounds were measured: phenyl methyl diketone ($M_\alpha = 41{\cdot}32$), benzoylformaldehyde ($M_\alpha = 36{\cdot}99$), *cis*-dibenzoylethylene (m. p. 111°; $M_\alpha = 73{\cdot}96$), *trans*-dibenzoylethylene (m. p. 134°; $M_\alpha = 71{\cdot}84$), *cis*-dibenzoylphenylethylene ($M_\alpha = 99{\cdot}57$), *cis*-dibenzoyldiphenylethylene ($M_\alpha = 122{\cdot}76$), *trans*-dibenzoyldiphenylethylene ($M_\alpha = 123{\cdot}71$). The evidence from a consideration of their refractive power is applied to determine the constitution of the α-diketones and *s*-diacylethylenes. Marked similarities are shown in the behaviour of these two classes of compounds.

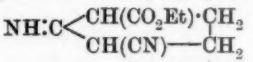
17. "The transformation of aliphatic nitriles into alicyclic imino-compounds." (Preliminary note.) By Jocelyn Field Thorpe.

For some time past, experiments have been in progress having for their object the study of the conditions under which aliphatic dinitriles having the nitrile groups separated by two, three, four, etc., carbon atoms pass into the corresponding alicyclic imino-compounds.

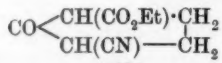
Preliminary experiments indicate that there is a greater tendency to form a three-carbon ring in this manner than a ring of four carbon atoms, but that the *cyclo*pentane ring is produced with most remarkable ease.

Thus, during some experiments on the formation of the *cyclo*propane ring by the interaction of ethyl sodiocyanoacetate and ethylene dibromide, Carpenter and Perkin (*Trans.*, 1899, **75**, 921) isolated, as a by-product, a substance which melted at 119·5°, and to which they assigned the formula $CN{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et$ (ethyl αδ-dicyanovalerate), owing to the fact that it yielded adipic acid on hydrolysis with alkaline hydrolysing agents.

It is now found that this substance is ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate (I), and that it is immediately converted by the action of cold concentrated hydrochloric acid into ethyl 3-cyano*cyclo*pentan-2-one-1-carboxylate (II):

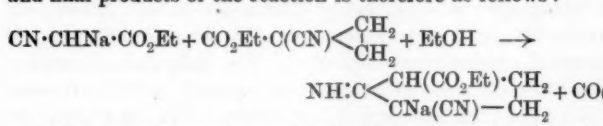


(I.)



(II.)

Ethyl 2-*imino*-3-*cyano*cyclo*pentane*-1-*carboxylate* can be produced in almost theoretical yield by the interaction of ethyl sodiocyanoacetate and ethyl 1-cyano*cyclo*propane-1-carboxylate in alcoholic solution, the sole products of the reaction being the sodium compound of the imino-compound and ethyl carbonate; the equation representing the initial and final products of the reaction is therefore as follows:



A similar condensation product is obtained when ethyl sodiomalonate is substituted for ethyl sodiocyanoacetate in the above equation. The investigation of the properties of these cyclic ketones is in progress.

18. "Action of alcohols on metallic calcium." By Frederick Mollwo Perkin and Lionel Pratt.

When calcium is added to alcohols reaction ensues and the alkyloxide, $Ca(OAlk)_2$, is produced (*Proc.*, 1907, **23**, 304). The reaction, however, is generally slow, but is greatly facilitated by heat. Calcium hydride reacts more readily than metallic calcium, but the product is less pure than when the metal is employed, owing to impurities in the calcium hydride. Calcium ethoxide is soluble in ethyl alcohol, and crystallises with two molecules of alcohol of crystallisation. Other alkyloxides are not so readily prepared, owing to their insolubility in the alcohols. Calcium ethoxide has been employed satisfactorily for organic condensations in place of sodium ethoxide.

19. "The condensation of oxymethylenecamphor with primary and secondary amino-compounds." By William Jackson Pope and John Read.

On condensing externally compensated α-phenylethylamine with *d*-oxymethylenecamphor, two stereoisomeric products are obtained, one from each of the optically active components of the primary base; a method is thus indicated for ascertaining whether a particular primary amino-compound is or is not externally compensated. The

two products exhibit marked mutarotation, and this is attributed to their conversion in solution into isodynamic mixtures.

d-Oxymethylenecamphor itself and its condensation products with aniline, *p*-toluidine, and *β*-naphthylamine exhibit mutarotation in various solutions and this is again attributed to isodynamic change.

20. "Note on the variation in the catalytic activity of mineral acids with changes in their concentration." By Arthur Lapworth.

Several recent investigations (Senter., *Trans.*, 1908, **91**, 467: Stieglitz, *Amer. Chem. J.*, 1908, **39**, 29 *et seq.*; Acree and others, *Ber.*, 1908, **41**, 3214 *et seq.*) suggest that during certain changes, in which electrolytes are concerned, not only simple and complex ions are directly concerned, but that intramolecular changes in, and interactions between, non-ionised substances may occur, and sometimes even to the extent of being a necessary part of the process.

The author recently referred to such a possibility in the case of esterification as accelerated by an acid (*Trans.*, 1908, **93**, 2196, 2197), inferring that the disproportionate increase in the velocity with increase in the amount of mineral acid may possibly be due to a secondary reaction of this nature. It is necessary to state that the discussion applied only to those cases where no relatively powerful base is present in such small quantity that this decreases rapidly on addition of mineral acid, as might conceivably be the condition in alcohol containing only a very little water; the general case, however, comes under the discussion mentioned, and, as has long been recognised, is doubtless intimately connected with neutral salt action.

Attention must also be drawn to the fact that the expression for $\frac{1}{2}\frac{d^2(H^2)}{dA^2}$ (*not* $\frac{d^2(H^2)}{dA^2}$: *loc. cit.*, p. 2197), which indicates the direction of change in relative quantity of non-ionised compounds with alteration in the amount of catalyst, is always positive, this not being limited even by the condition suggested.

21. "The condensation of dimethyldihydroresorcin with ethylamine." By Paul Haas.

By the action of nitrous acid on the condensation product of ethylamine with dimethyldihydroresorcin, a compound of the constitution

$$CMe_2\begin{<}CH_2\cdot C(:NEt)\\CH_2\text{——}CO\end{>}C:N\cdot OH$$

is produced.

This substance crystallises from water with two molecules of the solvent, and has a very intense carmine colour; when dried in a vacuum it becomes anhydrous, and is then dark blue.

ANNIVERSARY DINNER.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends, to be held at the Whitehall Rooms on Thursday, March 25th, 1909, this being the day fixed for the Annual General Meeting. Further particulars will be announced shortly.

ERRATA.

PROCEEDINGS, 1908.

Page.	Line.	
274	7	*for* "hypoiodate" *read* "hypoiodite."
280	20	title should be "**Silicon researches. Part XIII. Silicon halides and pyridine, acetonitrile, etc.**"

At the next Ordinary Meeting on **Thursday**, February **4th**, 1909, at **8.30** p.m., the following papers will be communicated :

"The triazo-group. Part VII. Interaction of benzhydroximic chloride and sodium azide." By M. O. Forster.

"The triazo-group. Part VIII. Azoimides of the monobasic aliphatic acids." By M. O. Forster and R. Müller.

"Nitro-derivatives of ortho-xylene." By A. W. Crossley and Miss Nora Renouf

"The divergence of the atomic weights of the lighter elements from whole numbers." By A. C. G. Egerton.

"Benzyl and ethyl derivatives of silicon tetrachloride." By G. Martin and F. S. Kipping.

"The constituents of the bark of *Prunus Serotina*. Isolation of l-mandelonitrile glucoside." By F. B. Power and C. W. Moore.

"The mechanism of the reduction of nitroanilines and nitrophenols." By B. Flürscheim.

"The relation between the strength of acids and bases, and the quantitative distribution of affinity in the molecule." By B. Flürscheim.

"A simple notation for indicating the configuration of the sugars and allied substances." By T. S. Patterson.

"Note on the determination of the rate of chemical change by measurement of the gases evolved." By F. E. E. Lamplough.

"The formation and reactions of imino-compounds. Part VIII. The formation of methyl derivatives of 1 : 3-diamino-2-phenylnaphthalene from the three tolylacetonitriles." By S. R. Best and J. F. Thorpe.

"The effect of conjugated unsaturated groups on optical activity. Part I." By T. P. Hilditch.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 13/2/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. **No. 351.**

Thursday, February 4th, 1909, at 8.30 p.m., SIR WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Mr. F. Williams was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs.:

Howard Alfred Caulkin, B.Sc., Oaklands, Solihull, Warwickshire.
John Henry Chew, 46, Lytham Road, Blackpool.
George Clarke, Cawnpore, U.P., India.
George Stanley Cooper, Heaton House, Cleckheaton, Yorks.
William Fowler, 3, Cranbrook Road, Victoria Docks, E.
Egerton Hargreaves, M.Sc., "Arthog," Garner's Lane, Davenport.
Reginald Hopkinson, B.Sc., Brimington House, Brimington.
Floyd J. Metzger, Columbia University, New York City, U.S.A.
Oswald John Dalgatty Thomas, 65, Clarendon Gardens, Ilford.
Vernon James Tilley, "Linthorpe," Becmead Avenue, Streatham, S.W.
Charles William Truelove, B.Sc., 17, Tylney Road, Forest Gate, E.
Robert William Wilson, 2, Parade, Aldersbrook Road, Manor Park, E.

Of the following papers, those marked * were read:

***22. "The mechanism of the reduction of nitroanilines and nitrophenols." By Bernhard Flürscheim.**

Flürscheim and Simon have shown recently that 2 : 4-dinitrodiphenylamine, on reduction by stannous chloride, only yields the amine

under conditions which cause the azoxy-derivative to be formed in the case of all the other dinitro-compounds examined. Similar observations in alkaline solutions had led Elbs to assume the following changes during the reduction of *o*- and *p*-nitroaniline and phenols:

$$C_6H_4\begin{cases}NH_2\\NH\cdot OH\end{cases} \longrightarrow C_6H_4\begin{cases}NH\\NH\end{cases} \longrightarrow C_6H_4\begin{cases}NH_2\\NH_2\end{cases}, \text{ etc.}$$

According to the views on substitution in aromatic compounds put forward by the present author, it seemed possible that, condensation to the azoxy-derivative being due to the residual affinity of the tervalent nitrogen in the hydroxylamine and nitroso-compounds, partial saturation of that residual affinity through the influence of an ortho- or para-amino- or hydroxyl group might prevent such condensation.

To decide this question, the behaviour of 2 : 4-dinitrodiphenylmethylamine was examined, intramolecular change being here excluded. It was found that, in this case also, no azoxy-compound, but only the amine, is formed. Experimental evidence, therefore, favours the second of the above hypotheses.

***23. "The relation between the strength of acids and bases and the quantitative distribution of affinity in the molecule." By Bernhard Flürscheim.**

It has been frequently observed that introduction of acidic or basic radicles into the molecule of an acid does not necessarily affect the dissociation constant in the expected sense, but often in the opposite direction. The author suggests the following hypothesis in explanation of this: The dissociation constant of an acid is inversely proportional to the strength of the bond between the acidic radicle and hydrogen, and directly proportional to the strength of the linking between the acidic radicle and the negative electron. The latter depends on the more or less negative nature of the acidic radicle; the former, however, is chiefly a function of the amount of affinity which the atom to which hydrogen is linked can place at the hydrogen's disposal. This amount is variable, and its order of magnitude can in each particular case be foreseen by the application of general views previously advanced by the author.

Similarly, quaternary ammonium hydroxides and analogous derivatives of oxygen, sulphur, iodine, etc., even when negatively substituted, may be strong electrolytes, because quinquevalent nitrogen can only weakly attract the hydroxyl group. Lastly, the salts of amines, etc., with acids are hydrolysed more readily when the nitrogen is linked to unsaturated atoms which absorb much of its affinity. A

consideration of many affinity constants, hitherto thought abnormal, confirms these views, which have also been experimentally supported by the discovery that, when the basic group ·NMePh is introduced in the ortho-position with respect to the amino-group of *m*-nitroaniline, the basicity of the latter is very considerably reduced.

***24. "Note on the determination of the rate of chemical change by measurement of the gases evolved." By Francis Edward Everard Lamplough.**

In a criticism of the author's work on this subject, J. C. Cain and F. Nicoll (*Proc.*, 1908, **24**, 282) have contended that the solutions of diazobenzene chloride, the rate of decomposition of which was being determined by them from the rate of evolution of nitrogen, did not become supersaturated by the gas, and that no error was thereby introduced into their results.

With regard to the statements of Cain and Nicoll, it is manifest that their treatment of the solution (shaking, etc.) *before* measurement could not possibly prevent supersaturation occurring whilst measurement was taking place. Secondly, the ultimate evolution of the calculated volume of gas from the solution is merely evidence that the condition of supersaturation is only a temporary one. This would be expected of a metastable state, and is fully shown to be the case from the author's experiments.

A very simple direct experiment is, however, the most convincing proof that their reasoning is inadmissible. If a solution of diazobenzene chloride, prepared in the usual manner and rapidly heated with or without shaking, say, to 50°, is allowed to stand for ten or fifteen minutes and the flask then gently revolved so as to set the liquid in fairly rapid rotation, a copious effervescence will at once be seen to result. The effect is still more clearly shown if the flask is connected to a pneumatic trough, in which case the liquid may be well agitated by shaking.

Experiments were made by the author which showed that under conditions of efficient stirring no acceleration of the reaction was produced by "colloidal" platinum. This is not surprising in view of the immediate precipitation of the metal from the colloidal state in the presence of the strong electrolytes contained in the solution.

In throwing doubt on the measurement of temperature, Cain and Nicoll appear entirely to have overlooked the experiment (*Proc. Camb. Phil. Soc.*, 1908, **14**, 590) by which it is proved that, throughout the time of measurement, the temperature of the reacting liquid did not differ more than 0·1° from that of the water-bath. A few words of a sentence from the author's paper are quoted apart from the context

by Cain and Nicoll, so that they produce an entirely incorrect impression as to the actual procedure.

Finally, no suggestion of errors in temperature measurements could possibly dispose of the obvious conclusions from the comparative experiments performed with and without stirring at the same temperature and in the presence of the same platinum stirrer. In the experiments *with* agitation of the solution, the gas was at first evolved with high velocity, and this rate gradually diminished, strictly following the unimolecular law. In those *without* agitation, the rate of evolution was at first slow, gradually increased to a maximum value, and then diminished; if the stirrer was set in motion at any time in such an experiment, the immediate evolution of the large quantity of stored-up gas indicated a degree of supersaturation up to 100 times the volume normally dissolved. Again, in the experiments with stirring, the values of the velocity constant from first to last showed only very slight and irregularly-distributed differences from the mean value; in the experiments without stirring, and in those of Cain and Nicoll, at best only a limited range from the middle of the experiment could be selected over which the calculated values of the "constant" (much lower than those of the experiments with stirring) might be plausibly uniform.

Discussion.

Dr. Veley remarked, with reference to the author's statement as to the rate of decomposition of oxalic by sulphuric acid, that it appeared unreasonable, if not romantic, to criticise work which he, the speaker, had never done, and conclusions at which he had never arrived.

From calculations made in a number of cases in which a gas is evolved from a solution by a process of chemical change, it appeared that the author had very greatly overestimated the supersaturation value as at 100, or even more; it probably did not exceed 8 to 12, according to the nature of the gas and conditions of experiment.

Mr. Lamplough, in reply, pointed out that Euler performed his one comparison experiment with and without stirring at 25°. At this temperature the velocity of the reaction would be 100 times less, and the solubility of nitrogen only twice greater, than at the temperature of his (the speaker's) comparison experiment then under consideration, and a much closer agreement would therefore be expected. The author had hitherto confined his attention to the benzenediazonium compounds, and these had been investigated at temperatures from 36° to 67°. Mr. Lamplough offered apologies to Dr. Veley for the

incorrect statement that he (Dr. Veley) had shown the decomposition of oxalic acid by sulphuric acid to be bimolecular. It should rather have been said that Dr. Veley found that the decomposition of formic acid by sulphuric acid was bimolecular, but had arrived at no conclusion from his experiments with oxalic acid (*Phil. Trans.*, 1888, **178**, 280, 291). Both these actions had since been shown to be unimolecular, the former by the author, the latter by Lichty, of Heidelberg, by a titration method. He further pointed out that his method of determining the degree of supersaturation was not theoretical, but practical, and confirmed his assertion as to the high degrees of supersaturation obtained by showing from the curves of an actual experiment that 37 c.c. of solution at 62° held at one time 21 c.c. of gas, which from the value 0·006 for the solubility of nitrogen at 62° represented a degree of supersaturation of more than 90. In justification of the words "plausibly uniform," an example was taken from Cain and Nicoll's paper (*Trans.*, 1902, **81**, 1416), from which it was shown that over a range of 15 per cent. of the reaction there was a continuous variation of the velocity constant amounting to 12·2 per cent. of its mean value, and the other experiment at the same temperature did not show a much greater constancy. He had, however, no intention of disputing that Cain and Nicoll had been able, owing to the very slight solubility of nitrogen, to show that the decomposition of diazobenzene chloride was possibly, even probably, a unimolecular action, but contended that the temporary state of supersaturation had seriously affected the values of their constants; in the case of actions which evolved more soluble gases, even the order of the reaction became untrustworthy. The crucial test of the development of this state was experiment, such as the simple one described above.

*25. **"The triazo-group. Part VII. Interaction of benzhydroximic chloride and sodium azide." By Martin Onslow Forster.**

5 : 1-*Phenylhydroxytetrazole*, $C_6H_5\cdot C\begin{matrix}N\text{——}N\\ \|\\ N(OH)\cdot N\end{matrix}$, is produced, instead of the expected benzhydroximic azoimide, when sodium azide and benzhydroximic chloride interact; it melts and decomposes at 124°, undergoing spontaneous decomposition in the course of a few days, and is resolved by alkalis into benzonitrile, nitrogen, and nitrous oxide. The *benzoyl*, *p-toluenesulphonic*, and *β-naphthalenesulphonic* derivatives are stable, however, decomposing at 127°, 91—92°, and 101° respectively.

***26. "The triazo-group. Part VIII. Azoimides of the monobasic aliphatic acids." By Martin Onslow Forster and Robert Müller.**

A description was given of α-triazobutyric, α-triazo*iso*butyric, and α-triazo*iso*valeric acids, their amides and ethyl esters, with further information concerning triazoacetic and α-triazopropionic acids, these compounds having been studied with the object of determining the influence of environment on the stability of the triazo-group in the series.

***27. "Nitro-derivatives of ortho-xylene." By Arthur William Crossley and Nora Renouf.**

In continuance of the work, briefly described in a preliminary note (*Proc.*, 1908, **24**, 58), the action of nitrating agents on *o*-xylene has now been thoroughly investigated, with the result that all the theoretically possible mono-, di-, and tri-nitro-*o*-xylenes have been prepared. The methods adopted in establishing the constitutions of the various nitro-*o*-xylenes were discussed.

***28. "The divergence of the atomic weights of the lighter elements from whole numbers." By Alfred Charles Glyn Egerton.**

The atomic weights of the first fifteen elements have been calculated according to a simple formula, in which a constant is multiplied by a constantly increasing whole number in order to obtain the divergence from whole numbers of the atomic weights. The atomic weights of the next thirteen elements have been calculated according to a slightly modified formula. The agreement is, in nearly all cases, to the second place of decimals. The relation suggests a modification of Prout's hypothesis.

Discussion.

The President said that he considered this as an epoch-making paper. The plan brought forward differed from all previous attempts to introduce regularity into the irregular series of numbers in the periodic table, inasmuch as it was based on a definite physical conception: the addition or subtraction of groups of electrons from the atoms; or, what came to much the same thing, definite amounts of electro-magnetic attraction which might conceivably alter mass.

***29. "The constituents of the bark of Prunus serotina. Isolation of *l*-mandelonitrile glucoside." By Frederick Belding Power and Charles Watson Moore.**

The material employed, consisting of the air-dried bark of *Prunus serotina*, Ehrhart, yielded on maceration with water an amount of hydrogen cyanide corresponding with about 0·075 per cent. of its weight. It has been shown to contain *l*-mandelonitrile glucoside, $C_{14}H_{17}O_6N$ (m. p. 145—147°; $[\alpha]_D$ – 29·6°), which has also been obtained in the form of its tetra-acetyl derivative (m. p. 136—137°; $[\alpha]_D$ – 24·0°), and an enzyme which hydrolyses β-glucosides. An alcoholic extract of the bark, on distillation with steam, yielded small amounts of benzoic acid and an essential oil, but no hydrogen cyanide. The non-volatile constituents of the bark consisted of a green resin, insoluble in either hot or cold water; a brown resin, soluble in the hot aqueous liquid, but deposited on cooling; and material which remained dissolved in the cold aqueous liquid. The green resin, amounting to about one per cent. of the weight of the bark, yielded a phytosterol, $C_{27}H_{46}O$ (m. p. 135—136°; $[\alpha]_D$ – 34·0°), palmitic, stearic, oleic, linolic, and *iso*linolenic acids, a little ipuranol, $C_{23}H_{38}O_2(OH)_2$, and, after acid hydrolysis, oleic acid, dextrose, and β-methylæsculetin, $C_{10}H_8O_4$. The brown resin, amounting to about one per cent. of the weight of the bark, yielded, after acid hydrolysis, traces of a phytosterol, small amounts of oleic acid, β-methylæsculetin, and dextrose, together with insoluble, red, resinous material. The portion of the alcoholic extract which was soluble in cold water contained the *l*-mandelonitrile glucoside, together with a quantity of sugar and tannin. It yielded, furthermore, benzoic, trimethylgallic, and *p*-cumaric acids, traces of a substance melting at 240—241°, and, after heating with dilute sulphuric acid, *l*-mandelic acid and β-methylæsculetin were obtained.

30. "Benzyl and ethyl derivatives of silicon tetrachloride." By Geoffrey Martin and Frederic Stanley Kipping.

The authors have made a study of certain benzyl- and ethyl-silicon compounds with the object of comparing their chemical behaviour with that of corresponding carbon compounds.

Tribenzylsilicon chloride and benzylsilicon trichloride, prepared by an improved method of applying the Grignard reagent, were decomposed by water, *tribenzylsilicol*, $Si(CH_2{\cdot}C_6H_5)_3{\cdot}OH$, and *benzylmetasilicic acid*, $C_6H_5{\cdot}CH_2{\cdot}SiO{\cdot}OH$, respectively being obtained. The

former when boiled with concentrated hydrochloric acid or with dilute aqueous potassium hydroxide is converted into *tribenzylsilicyl oxide*, $[(C_6H_5\cdot CH_2)_3Si]_2O$, a change not brought about by heating the silicol alone or with acetic anhydride; acetic chloride and benzoic chloride convert the silicol into the corresponding chloride. *Tribenzylsilicyl oxide* is a colourless solid, m. p. 205°, soluble in chloroform, but sparingly so in light petroleum or alcohol.

Benzylmetasilicic acid, a resinous substance soluble in ether, does not exhibit properties analogous to those of a carboxylic acid; although soluble in potassium hydroxide solution, it does not form stable salts with organic bases. Its *ortho*-ester, $C_6H_5\cdot CH_2\cdot Si(OEt)_3$, and the *oxide*, $[C_6H_5\cdot CH_2\cdot Si(OEt)_2]_2O$, were prepared by treating benzylsilicon trichloride with ethyl alcohol; both are oils, boiling at 170—175°/(70 mm.) and 256—260°/(75 mm.) respectively. Attempts to prepare derivatives of silicon hexachloride by heating tribenzylsilicyl chloride, benzylsilicyl trichloride, and benzylethylpropylsilicyl chloride respectively with sodium or potassium were unsuccessful.

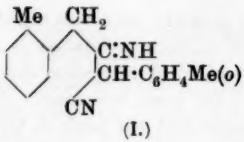
Diethylsilicon dichloride was prepared from silicon tetrachloride by the Grignard reaction, but the yield was very poor; under certain conditions a considerable proportion of the tetrachloride gives non-volatile products, from which, after treatment with water, a yellow powder may be obtained; this substance is soluble in alkali hydroxides with evolution of hydrogen, but insoluble in all other ordinary solvents, and seems to have the composition $C_2H_3O_8Si_2$.

Diethylsilicon dichloride is decomposed by water, giving a polymerised oily *silicone*, $(SiEt_2O)_n$; the hydrol, $SiEt_2(OH)_2$, apparently is not formed.

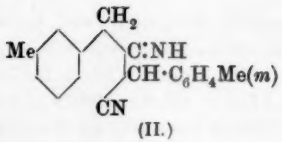
31. "The formation and reactions of imino-compounds. Part VIII. The formation of methyl derivatives of 2-phenyl-1 : 3-naphthylenediamine from the three tolylacetonitriles." By Stanley Robert Best and Jocelyn Field Thorpe.

Previous experiments have indicated that the transformation of a benzenoid imino-nitrile into a derivative of 1 : 3-naphthylenediamine by the action of cold concentrated sulphuric acid is hindered if a methyl group is in the meta-position with respect to the carbon atom at which ring formation must take place. Experiments have now been made which furnish further instances of this hindering action.

The three tolylacetonitriles readily undergo intramolecular condensation, forming *β-imino-α-cyano-αγ-di-o-tolylpropane* (I), *β-imino-α-cyano-αγ-di*-m-*tolylpropane* (II), and *β-imino-α-cyano-αγ-di*-p-*tolylpropane* (III):



(I.)



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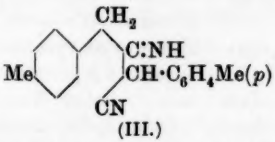
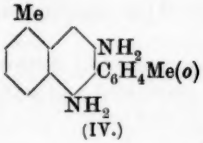
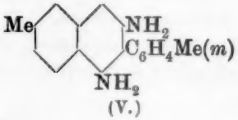


(III.)

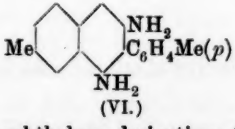
and when these compounds are treated with cold concentrated sulphuric acid they are converted into the sulphates of 6-o-*tolyl*-1-*methyl*-5 : 7-*naphthylenediamine* (IV), 6-m-*tolyl*-2-*methyl*-5 : 7-*naphthylenediamine* (V), and 7-p-*tolyl*-2-*methyl*-6 : 8-*naphthylenediamine* (VI) respectively :



(IV.)



(V.)



(VI.)

The yields of the naphthalene derivatives from the three iminonitriles are in accordance with previous observations. Thus the meta-derivative (II), from which ring formation is shown by the oxidation of the naphthalene derivative to 4-methylphthalic acid to take place in the para-position with respect to the methyl group, gives 80 per cent. of the theoretical quantity of 6-*m*-tolyl-2-methyl-5 : 7-naphthylenediamine (V), whereas from the ortho- and para-derivatives (I and III), from which ring formation has to take place in the meta-position with respect to the methyl group, scarcely more than 10 per cent. of the naphthalene derivatives (IV and VI) are obtained under the same experimental conditions. The preparation and properties of the pyrimidine derivatives derived from the three tolylacetonitriles were described.

32. "The effect of contiguous unsaturated groups on optical activity. Part I." By Thomas Percy Hilditch.

The chemical and physical behaviour of organic substances containing adjacent unsaturated groups has frequently been observed to

be irregular, and, as is well known, the optical properties of refractive index and magnetic rotatory power exhibit anomalies in such cases. The present work is the first part of an investigation designed to find out if optical activity is subject to the same influences. From the collected observations of different workers, in the cases of terpene derivatives, optically active aromatic substances and optically active esters possessing conjugated unsaturated systems, the author showed that in many, but not in all, instances a pronounced increase in molecular rotatory power takes place. Further, from observations on the camphorates and camphor-β-sulphonates of a number of phenolic or amino-derivatives of substances containing a benzenoid residue adjacent to an ethylenic or carbonyl group, it is found that:

(1) Conjugation is accompanied by abnormal optical activity.

(2) The effect reaches a maximum when the conjugated system is nearest to the asymmetric carbon atoms.

(3) The effect is lessened as the proximity of the unsaturated groups to one another is lessened.

(4) The effect is decreased, and sometimes completely destroyed, if a saturated group is interposed between the conjugated and asymmetric systems.

33. "The miscibility of solids." By Ernest Vanstone.

While working on solid solutions with camphor, the author was led to develop the present theory. The explanation of the miscibility of solids is suggested by the Pope and Barlow theory, and may be stated as follows: Two substances will show the greatest degree of miscibility, whose assemblages of spheres of atomic influence possess similar marshalling, and are capable of being partitioned into units possessing almost equal volumes, the volumes being the molecular domains.

This explanation applies to the miscibility of the elements and of compounds, both organic and inorganic.

The degree of miscibility of two elements depends on the closeness of agreement between the atomic volumes, and also on their valency values, and this accounts for the great tendency of the elements to form mixed crystals.

Where a difference in valency volumes exists, a slight expansion of the spheres composing the substance of lower valency volume causes the volume of the molecular unit to approximate closely to that of the substance of higher valency volume.

The freezing-point curves for camphor and borneol, benzoin and benzil, and menthol and menthone have been obtained. The first

pair of compounds forms solid solutions in all proportions, borneol raising the freezing point of camphor continuously. Benzoin and benzil show a curious behaviour, as the curve has two eutectic points with an intermediate horizontal portion. The curve for menthol and menthone appears to be continuous with a minimum point.

34. "Esterification constants of substituted acrylic acids. Part III." By John Joseph Sudborough and James Mylam Gittins.

The constants at 15°, using methyl alcohol with hydrogen chloride as catalyst, have been determined for the following acids: *cyclo*-Hexanecarboxylic; phenylacetic, α- and β-phenylpropionic, γ-phenyl-*n*-butyric, δ-phenyl-*n*-valeric, furfurylpropionic, phenylbenzylacetic, undecylenic, oleic, elaidic, erucic, brassidic, phenyl-βγ-crotonic, allylacetic, sorbic, cinnamylideneacetic, hydrosorbic, cinnamenylpropionic, β-phenylethylidenepropionic, phenylpropylideneacetic, αβ-oleic, *allo*-cinnamic, and tetrolic. The results confirm the conclusions previously drawn (*Trans.*, 1905, **87**, 1840; 1907, **91**, 1033).

The constants for αβ-unsaturated acids are remarkably low when compared with those for the corresponding saturated acids. βγ-Unsaturated acids have constants somewhat larger than those for their saturated analogues, and double bonds which are still further removed from the carboxylic group have very little effect, so that there is practically no difference between the constants for the unsaturated and the corresponding saturated acid.

The effect of the reduction of benzoic to *cyclo*hexanecarboxylic acid is remarkable, the constant being raised from 0·25 to 19·3.

A triple linking in the αβ-position has much the same effect as a double bond in the same position, and conjugate ethylene linkings have a somewhat greater retarding effect than an αβ-double linking.

35. "Brazilin, hæmatoxylin, and their derivatives. Part X. The constitution of trimethylbrazilone, of α- and β-anhydrotrimethylbrazilone, and of the corresponding derivatives of hæmatoxylin." By William Henry Perkin, jun., and Robert Robinson.

The authors described in detail the properties of the derivatives mentioned in the title with the object of proving that the constitutional formulæ assigned to them in the previous parts of this research are correct.

36. "The preparation of disulphides. Part III. The nitrobenzyl disulphides. (A correction.)" By Thomas Slater Price and Douglas Frank Twiss.

In a recent communication on the nitrobenzyl disulphides (*Trans.*, 1908, **93**, 1401), the statement was made that "the three disulphides obtained in the course of this investigation have not been isolated before." This statement is erroneous so far as the ortho- and meta-disulphides are concerned, but it does not affect the subject-matter of the paper cited, since a new method of preparation of these disulphides is there given.

Jahoda (*Monatsh.*, 1890, **10**, 874) claimed to have prepared di-*o*-nitrobenzyl disulphide (this nomenclature is to be preferred to *o*-nitrobenzyl disulphide), but Gabriel and Stelzner (*Ber.*, 1896, **29**, 161) showed that Jahoda's product was really the mercaptan. They prepared the *o*-disulphide and found it to consist of yellow crystals which melted at 112—113°, these properties agreeing with those found by Gabriel and Posner (*Ber.*, 1895, **28**, 1025) and Cassirer (*Ber.*, 1892, **25**, 3029). In 1901, Blanksma (*Rec. trav. chim.*, 1901, **20**, 137) also prepared di-*o*-nitrobenzyl disulphide (this compound is not mentioned in *Abstr.*, 1901, **80**, i, 461) and found that it melted at 110°. This melting point agrees with that observed by the authors (109·5°), but they also find that on repeated crystallisation from alcohol the crystals become almost colourless, possessing only a slight yellow tinge.

Di-*m*-nitrobenzyl disulphide has been prepared by Lutter (*Ber.*, 1897, **30**, 1069) by oxidation of the corresponding mercaptan with iodine, and is described as consisting of yellowish-white crystals melting at 103—104°. The melting point agrees with that observed by the authors, but when pure the substance is almost colourless; individual crystals appear colourless, but in bulk they possess a faint yellow tinge.

Strakosch (*Ber.*, 1872, **5**, 692) claims to have obtained di-*p*-nitrobenzyl disulphide. The melting point given, 89°, is quite different from that observed by the authors (126·5°), and does not correspond with the melting points of the *o*- and *m*-compounds. The analytical results are also not satisfactory, 19·72 per cent. of sulphur being found instead of 19·05 per cent. Evidently the compound prepared by Strakosch was not the disulphide, and the authors are engaged in repeating his experiments. The pure substance possesses a colour similar to that of the *m*-disulphide.

37. "Derivatives of naphthacenequinone. Part III." By Dorothy Harrop, Roland Victor Norris, and Charles Weizmann

In continuation of previous work (*Trans.*, 1907, **91**, 1588), the authors have prepared a further series of naphthacenequinone derivatives.

38. "The nature of ammoniacal copper solutions. Part II. The solubility of cupric hydroxide in ammoniacal sulphate solutions." By Harry Medforth Dawson.

With the object of supplementing the information already obtained concerning the nature of ammoniacal solutions of copper salts (compare Dawson, *Trans.*, 1906, **89**, 1666; 1900, **77**, 1239), the author has measured the solubility of cupric hydroxide in ammoniacal solutions of ammonium and sodium sulphates, and of barium and sodium hydroxides.

Cupric hydroxide does not dissolve directly in pure ammonium sulphate solutions, and this is an indication that cupridiammonia compounds either do not exist or are not readily formed. In presence of ammonia the hydroxide dissolves readily, and ammonia therefore appears to be the primary cause of the solution process, cupritetra-ammonia hydroxide being thereby formed. This then reacts with the ammonium sulphate in the solution, the action consisting in the partial displacement of the ammonia from the sulphate by the stronger cupri-ammonia base, a condition of equilibrium being set up corresponding with the scheme:

$$Cu{\cdot}4NH_3(OH)_2 + (NH_4)_2SO_4 \rightleftarrows Cu{\cdot}4NH_3SO_4 + 2NH_4OH.$$

The solubility data are consistent with this view.

From a consideration of the quantities of ammonia which are necessary to dissolve cupric hydroxide in such quantity that the resulting solution contains copper and sulphate in equivalent proportions, the conclusion is drawn that optically clear solutions, prepared by adding ammonia (not in large excess) to copper sulphate solutions, are supersaturated with respect to cupric hydroxide. When such solutions are shaken with cupric hydroxide, a diminution in the copper concentration is actually observed. The deposited copper is supposed to be present in the original solution in the form of colloidal hydroxide.

The new observations are in agreement with the author's previous determinations of the chemical dissociation in ammoniacal solutions of copper salts on the basis of distribution measurements.

39. "The action of β-rays on photosensitive solutions." By Otto Flaschner.

The analogy between the action of light and that of β-rays on certain chemical reactions was pointed out and instanced in the case of two photosensitive solutions. The potential of an AgBr/KBr electrode rises under the influence of β-rays, and falls when the latter disappear. The higher the initial potential the more sensitive is the electrode towards light and β-rays.

The Eder's actinometric solution was the second type to be examined, and this is also influenced by β-rays.

40. "The rusting of iron." By Gerald Tattersall Moody.

In the experiments described by Tilden (*Trans.*, 1908, **93**, 1356), that author has lost sight of the well-known fact that commercial iron and steel invariably contain foreign substances, notably sulphur compounds, which on exposure to air and water at once furnish free acids. The rusting observed in Tilden's experiments, in which carbonic acid was excluded, was a result primarily of interaction between acids, formed by oxidation of sulphur compounds and other foreign constituents capable of furnishing acids on reaction with water and oxygen, and iron, the resulting ferrous salt being subsequently oxidised with production of rust.

Tilden's experiments conclusively show that commercial iron after treatment with chromic acid no longer rusts in presence of water and oxygen, but the inactivity is wrongly attributed to the chromic acid rendering the iron "passive." The true explanation of the inhibitive effect of chromic acid is that it removes from the surface of the iron those constituents which would otherwise subsequently yield acids on exposure to water and oxygen. That Tilden's view that the iron is rendered passive is incorrect is conclusively shown by the readiness with which the iron rusts as soon as normal air containing carbonic acid or any other acid is admitted.

Tilden further states that after immersion for years of iron in dilute chromic acid, he has observed "no sign of rust or of dissolution of the iron either by change of colour or the formation of precipitate on adding excess of ammonia." In this connexion it must be pointed out that ferric hydroxide is readily dissolved by chromic acid, so that visible change could not be expected. Moreover, dilute solutions of iron in chromic acid do not afford a visible precipitate or a change of colour on addition of excess of ammonia. If, however,

the solution is filtered after addition of ammonia, ferric hydroxide in appreciable quantity remains on the filter-paper, and the dissolution of the iron is thereby made evident.

41. "The iodobenzenemonosulphonic acids. Part I." By Mary Boyle.

An account was given of the preparation and properties of 1 : 4 : 6-, 1 : 3 : 4-, 1 : 3 : 5-, and 1 : 2 : 4-*di-iodobenzenesulphonic acids*; also of 1 : 2 : 3 : 5-, 1 : 2 : 4 : 5-, and 1 : 2 : 4 : 6-*tri-iodobenzenesulphonic acids*. The acids were mostly prepared from the appropriate aminosulphonic acids by introducing iodine by means of iodine chloride and subsequently displacing the amino-group by iodine by the diazo-reaction.

It is noteworthy that all the iodo-diazo-sulphonates are coloured compounds, varying from very pale yellow in the case of the 1 : 4-acid to bright yellow in the case of the tri-iodo-acids.

The acids are all readily soluble in water, and several crystallise well, especially in presence of mineral acid. They furnish well-defined salts, which are only sparingly soluble in water. The sulphonyl chlorides crystallise well.

42. "Contributions to the chemistry of the terpenes. Part IV. The oxidation of pinene with mercuric acetate." By George Gerald Henderson and James Watson Agnew.

By the action of aqueous mercuric acetate at the ordinary temperature, pinene is converted into sobrerol, $C_{10}H_{16}(OH)_2$, a compound formerly prepared by oxidising pinene with moist oxygen in sunlight, and sobrerol is oxidised to a hydroxyketone, $C_{10}H_{15}(OH)O$, when heated with the same reagent. The hydroxyketone is reduced to sobrerol when dissolved in moist ether and treated with sodium, and it yields carvacrol on reduction with aqueous hydriodic acid in the cold. When heated for a short time with anhydrous oxalic acid, it yields carvone together with some carvacrol, and when it is oxidised with an acidified solution of potassium permanganate, terpenylic acid is obtained. Hence it is concluded that the hydroxyketone is 8-hydroxycarvotanacetone.

Sobrerol can also be prepared by the action of mercuric oxide on a cold solution of pinene in acetic acid, whilst if the solution is heated, the oxidation product is the hydroxyketone.

43. "Formation of heterocyclic compounds. Part I. 1-Phenylpyrrolidine-2:5-dicarboxylic acid from adipic acid." By Henry Rondel Le Sueur.

The *methyl* or *ethyl* ester of 1-phenylpyrrolidine-2:5-dicarboxylic acid is readily obtained by the action of monoethylaniline on the corresponding methyl or ethyl ester of *aa'*-dibromoadipic acid.

1-*Phenylpyrrolidine*-2:5-*dicarboxylic acid* is crystalline, and decomposes at 252°; it is readily obtained by hydrolysis of its ethyl ester.

44. "The influence of solvents on the rotation of optically active compounds. Part XIV. Ethyl tartrate in benzaldehyde and in quinoline." By Thomas Stewart Patterson and David Paterson McDonald.

The influence of benzaldehyde and of quinoline as solvents on the rotation of ethyl tartrate was described.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Académie des Sciences, Paris. Comptes rendus hebdomadaires des séances de l'Academie. Vol. lxxiv—lxxxv. 12 vols. Paris 1872–77. (*Circulating.*) From Dr. Horace T. Brown.

Archibald, *R. D.*, and **Rankin,** *R.* Electrical laboratory course. pp. vi + 95. ill. London 1908. (*Recd.* 20/11/08.)
From the Publishers: Messrs. Blackie & Son.

Browning, *Philip E.* Introduction to the rarer elements. 2nd edition. pp. x + 207. New York 1908. (*Recd.* 5/1/09.)
From the Publishers: Messrs. John Wiley & Sons.

Dannerth, *Frederic.* The methods of textile chemistry. pp. viii + 164. New York 1908. (*Recd.* 27/11/08.)
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Donnan, *Frederick George.* Kupfer und seine Verbindungen. [Abegg's Handbuch der Anorganischen Chemie. II. i.] pp. 469 to 654. (*Recd.* 12/1/09.) From the Author.

Dunstan, *Albert Ernest.* An organic chemistry for schools and technical institutes. pp. viii + 160. ill. London 1908. (*Recd.* 10/11/08.) From the Publishers: Messrs. Methuen & Co.

Johnson, *Grove.* The student's manual of yeast culture. pp. xv + 180. ill. London 1908. (*Recd.* 10/11/08.) From the Author.

Kissling, *Richard.* Das Erdöl, seine Verarbeitung und Verwendung. Eine gedrängte Schilderung des Gesamtgebietes der Erdöl-Industrie. pp. x + 154. ill. Halle a. S. 1908. (*Recd.* 4/1/09.) From Dr. J. Lewkowitsch.

Lewkowitsch, *Julius.* Technologie et analyse chimiques des huiles, graisses et cires. Traduit . . . par *Émile* **Bontoux.** Tome II. pp. xiii + 563 to 1423. ill. Paris 1909. (*Recd.* 14/1/09.) From the Author.

Lunge, *George.* Technical chemists' handbook. Tables and methods of analysis for manufacturers of inorganic chemical products. pp. xv + 260. ill. London 1908. (*Recd.* 5/12/08.) From the Author.

Mathewson, *C. H.* First principles of chemical theory. pp. vii + 123. New York 1908. (*Recd.* 5/1/09.) From the Publishers: Messrs. John Wiley & Sons.

Morgan, *J. Livingston R.* The elements of physical chemistry. 4th edition. pp. xiv + 539. New York 1908. (*Recd.* 27/11/08.) From the Publishers: Messrs. John Wiley & Sons.

Pharmaceutical Society of Great Britain. Catalogue of the Library. 9th edition. Compiled by *John William* **Knapman.** pp. 715. London 1905. (*Reference.*) From the Society.

Plimmer, *R. H. Aders.* The chemical constitution of the proteins. In 2 parts. pp. xii + 100, xi + 66. London 1908. (*Recd.* 28/11/08.) From the Publishers: Messrs. Longmans, Green & Co.

Richards, *Ellen H.* Laboratory notes on industrial water analysis. pp. iii + 49. New York 1908. (*Recd.* 5/1/09.) From the Publishers: Messrs. John Wiley & Sons.

Roscoe, *Sir Henry Enfield,* **and Schorlemmer,** *Carl.* A treatise on chemistry. Vol. II. The metals. New edition, completely revised by *Sir H. E.* **Roscoe** and *A.* **Harden.** pp. xvi + 1436. ill. London 1907. (*Recd.* 19/12/08.) From Sir H. E. Roscoe.

Royal Society. Some account of the "letters and papers" of the period 1741–1806 in the archives. With an index of authors. Compiled by *A. H.* **Church.** pp. 73. Oxford. Printed for the author. 1908. (*Recd.* 9/12/08.) From Professor A. H. Church.

Société chimique de France. Cinquantenaire. pp. iv + 146. (42 plates.) Paris 1908. (*Reference.*) From the Society.

Turner, *Thomas.* The metallurgy of iron. pp. xvi + 463. ill. London 1908. (*Recd.* 3/12/08.) From Professor W. A. Tilden.

Woburn Experimental Fruit Farm. Ninth report. By the **Duke of Bedford** and *Spencer U.* **Pickering.** pp. 95 + xlvii. ill. London 1908. (*Recd.* 19/12/08.) From the Authors.

II. *By Purchase.*

Bowman, *Frederic Hungerford.* The structure of the cotton fibre in its relation to technical applications. pp. xx + 470. ill. London 1908. (*Recd.* 19/12/08.)

—— The structure of the wool fibre and its relation to the use of wool for technical purposes. pp. xx + 475. London 1908. (*Recd.* 19/12/08.)

Lundén, *Harald.* Affinitätsmessungen an schwachen Säuren und Basen. (Sammlung, Vol. XIV.) Stuttgart 1908.

Squire, *Peter Wyatt.* Companion to the latest edition of the British Pharmacopœia, comparing the strength of its various preparations with those of the United States, and other foreign pharmacopœias, to which are added not official preparations, and practical hints on prescribing. 18th edition. pp. xlii + 1417. London 1908. (*Recd.* 17/12/08.)

Watt, *Sir George.* The commercial products of India. Being an abridgement of "The dictionary of economic products of India." pp. viii + 1189. London 1908. (*Recd.* 17/12/08.)

Wiley, *Harvey W.* Principles and practice of agricultural analysis. Vol. II. Fertilizers and insecticides. pp. xi + 680. ill. Easton, Pa. 1908. (*Recd.* 3/12/08.)

Zeitschrift für anorganische Chemie. Generalregister der Bände 1—50 (1892–1906). pp. xxiv + 652. Hamburg 1908. (*Reference.*)

III. *Pamphlets.*

Ghose, *Anu.* The mode of occurrence of manganite in the manganese ore deposits of the Sandur State, Bellary, Madras, India. (From the *Trans. Inst. Min. Eng.*, 1908.)

India. *Imperial Department of Agriculture.* Report for the years 1905–06 and 1906–07. Calcutta 1908.

Jackson, *A. Hendrick.* The lead accumulator electrolyte. [1908.]

Lett, *Stephen J.* More about Zambesia minerals. (From the *Mining Journal*, 1908.)

Meininger, *Ernst.* Beitrag zur Kenntnis einiger Gummiarten. Mülhausen, 1908.

Mielck, *Wilhelm.* Pharmakognostisch-chemische Untersuchung des javanischen Lackharzes "Gala-Gala." Strassburg 1908.

Rathje, *Arnold.* Neuere Untersuchungen der Fette von Lycopodium, Secale cornutum, Semen Arecae und Semen Aleuritis cordatae sowie der brasilianischen Pflanzenmilch Amapa. Kiel 1908.

Siebeck, *Adolf.* Ueber einige organische Eisensalze. Wattenscheid 1908.

Simmer, *August.* Ueber das Verhalten der Alkaloidsalze und anderer organischer Substanzen zu den Lösungsmitteln der Perforationsmethode, insbesondere Chloroform, sowie über Reduktionswirkungen der Alkaloide. Strassburg 1906.

Sommerfeldt, *Ernst.* Thermochemische und thermodynamische Methoden, angewandt auf den Vorgang der Bildung von Mischkrystallen. Stuttgart 1900.

—— Petrographisch-chemische Untersuchungen an den Basalten des südlichen Bakony. Budapest 1908.

Transvaal. *Government Laboratories.* Annual Report for the year 1906–7. Pretoria 1908.

Weiss, *Hermann.* Pharmakognostische und phytochemische Untersuchung der Rinde und der Früchte von Aegiceras majus G., mit besonderer Berucksichtigung des Saponins. Strassburg 1906.

Wentrup, *Franz.* Beiträge zur Kenntnis der Saponine. Strassburg 1908.

West Indies. *Imperial Department of Agriculture.* Sugar-cane experiments in the Leeward Islands. Report on experiments conducted . . . in the season 1906–7. 2 parts. Barbados 1908.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Metropole, at 6.30 for 7 o'clock, on Thursday, March 25th, 1909 (the day fixed for the Annual General Meeting).

The price of the tickets will be One Guinea each, including wine.

All applications for tickets must be received not later than Thursday, March 18th next.

Tickets will be forwarded to Fellows on receipt of a remittance for the number required, made payable to "Mr. S. E. Carr" and addressed to the Assistant Secretary, Chemical Society, Burlington House, W.

At the next Ordinary Meeting on **Thursday**, February **18th**, 1909, there will be a ballot for the election of Fellows and the following papers will be communicated :

"A study of some asymmetric compounds." By F. S. Kipping.

"The decomposition and sublimation of ammonium nitrite under the influence of heat." By P. C. Rây.

"The estimation of hydroxyl derivatives in mixtures of organic compounds." By H. Hibbert.

"A simple method for determining the chemical affinity of organic substances." By H. Hibbert.

"The isolation of the aromatic sulphinic acids." By J. Thomas.

"Analytical investigation of zirconium metal." By E. Wedekind and S. Judd Lewis.

"Chlorine generated by potassium permanganate, its preparation and purity." By E. Wedekind and S. Judd Lewis.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, February 18th, 1909.

Adlam, George Henry Joseph,

86, Southmoor Road, Oxford.

Science Master, Boys' High School, Oxford. B.A. (Oxford). First-class in School of Natural Science, 1905 (Chemistry). Engaged in research in collaboration with Dr. H. B. Baker.

William Odling. W. W. Fisher.
H. B. Baker. C. Stanley Gibson.
J. E. Marsh.

Brunskill, Hubert,

7, Friarage Gardens, Hartlepool, Durham.

Teacher (Secondary). Inter.B.Sc. (London); Honours, Chemistry. Three years Science Teacher. I wish to join in order that I may keep up to date in chemical science, which I find rather difficult here; and also that at some future period I may contribute work on organic or physical chemistry.

Fred. Phillips. W. T. L. Leeming.
J. H. Howgate. W. H. Hurtley.
J. W. Patterson. *Sidney Harvey.*

Clayton, Arthur,

35, Sisters Avenue, Clapham Common, S.W.

Teacher of Chemistry. Author of "The Residual Affinity of the Coumarins," *J.C.S.*, 1908, and "The Coumarin Condensation," 1908. B.Sc., Hon. (London).

William A. Tilden. G. T. Morgan
James C. Philip. M. O. Forster.
Chapman Jones.

Cocksedge, Herbert Edwin,

5, Romola Road, Herne Hill, S.E.

Research Student. B.A. Final Honours Chemistry, Oxford, 1907 (1st); qualified for B.Sc. by research (Oxon.), 1908.

H. Brereton Baker. N. V. Sidgwick.
Andrea Angel. F. D. Chattaway.
J. E. Marsh.

Coles, Alfred Bertram,

42, Broadwater Road, Tottenham, N.

Science Master, Tottenham County School; Lecturer, Tottenham Polytechnic. M.A. (Oxon). Second Class Honours in Chemistry in Final School of Natural Science, Oxford, 1904. Science Master, Carmarthen Grammar School, 1904–1907. Sept. 1907: Senior Science Master, Tottenham County School, and Lecturer in Chemistry at Tottenham Polytechnic.

Andrea Angel. J. E. Marsh.
H. B. Baker. W. W. Fisher.
R. de J. Fleming Struthers.

Coope, John Charles Jesser,

Bulawayo, Rhodesia, South Africa.

Farmer. Diploma of the British Dairy Farmers' Association for proficiency in dairying and dairy farming; National Diploma (of England) for proficiency in science and practice of dairying; is an ex-student of British Dairy Institute and University College, Reading. Proposes to carry on investigations in dairying and agriculture in South Africa.

John W. Taylor. J. Augustus Voelcker.
J. F. Blackshaw. *Fredk. J. Lloyd.*
C. W. Walker Tisdale. *J. K. H. Inglis.*
E. K. Hanson.

Dunn, Frederick Percy,

Haresfield, Chorley Wood, Herts.

Research Student at the Royal College of Science. Educated at the Mercers' School; completed the Associateship Course in Chemistry at the Royal College of Science; Bachelor of Science (Lond.), Honours in Chemistry.

William A. Tilden. James C. Philip.
M. O. Forster. G. T. Morgan.
Taylor Cook.

Ferraboschi, Frederic,

Clare College, Cambridge.

Assistant Demonstrator at Cambridge University; engaged in research. Late scholar of Clare College, Cambridge. Paper on "A Double Sulphate of Guanidine and Aluminium" (*Proc. Camb. Phil. Soc.*, 1908, p. 471).

H. J. H. Fenton. H. O. Jones.
W. J. Sell. F. W. Dootson.
J. E. Purvis.

Fox, John Thomas,

Glen Burn, Stollard Street, Clay Cross, near Chesterfield.

A student and intending Science Master. Intermediate B.Sc., London, obtained two years ago last July, that is 1906. I have just finished a term of four years at the University College, Nottingham, the last two years of which have been occupied in preparation for the Honours B.Sc. in Chemistry of the London University, and I desire to follow the latest researches to continue the preparation.

Fredk. Cowling. F. Stanley Kipping.
Harry J. Unwin. R. M. Caven.
A. H. Salway.

Francis, Arthur Gordon,

50, Whitbread Road, Brockley, S.E.

Analyst in the Government Laboratory. Bachelor of Science (Hons.), London University. Fellow of the Institute of Chemistry. Six years' experience in the Government Laboratory under Dr. Thorpe, F.R.S., Mr. E. Grant Hooper, F.I.C., and Mr. W. T. Burgess, F.I.C.

T. E. Thorpe. James C. Philip.
E. Grant Hooper. G. T. Morgan.
William A. Tilden. William T. Burgess.
M. O. Forster. Charles A. Keane.

Furnell, John Thomas,

Acacia House, 32, Grosvenor Park Road, Walthamstow, Essex.

Paint and Colour-Mill Room Manager; practical experience extending twenty-five years. Registered as Technical Teacher, City and Guilds of London Institute. Ten years Teacher at the Polytechnic, Regent Street, W., in Painters' Colours, Oils, and Varnishes. Author of "Students' Handbook"; one of the Founders of the Paint and Varnish Society, London.

J. Cruickshank Smith. *C. Sordes Ellis*
Frank E. Weston. *H. R. Ellis.*
William A. Colebourn. *W. H. Collier.*

Gortner, Ross Aiken,

Lincoln, Nebraska, U.S.A. Present Address: 430, West 118th Street, New York City, U.S.A.

Fellow in Chemistry, Columbia University, New York City. B.Sc., Nebraska Wesleyan University, 1907. M.A., University of Toronto, 1908. Assistant in Chemistry, Nebraska Wesleyan University, 1904–6. Research Assistant in Chemistry, University of Nebraska, 1906–7. Assistant in Chemistry, University of Toronto, 1907–8. Fellow in Chemistry, Columbia University, New York City, 1908–9. Author of "Some Effects of Sunlight upon Colourless Glass," *Am. Chem. Jour.*, 157 (1908). Joint author of "Ueber Zwei Aromatische Nitrosoverbindungen," *Ber.*, **38**, 1899 (1905). "The Condensation of the Three Nitranilines with *p*-Nitroso-benzaldehyde," *Am. Chem. Jour.*, **36**, 510 (1906). "The Molecular Weights of the Yellow Nitroso-compounds," *Am. Chem. Jour.*, **32**, 400 (1904). "Soils of the Great Plains Region—The Third Steppe," *Am. Chem. Jour.*, **37**, 1 (1907). "The Detection of Bleached Flours," *Jour. Am. Chem. Soc.*, **29**, 1503 (1907). "Studies on Some Soils from Saskatchewan," *Am. Chem. Jour.*, **39**, 163 (1908). "Some Esters of Arsenious Acid," *Trans. Chem. Soc.*, **93**, 1364 (July, 1908).

W. R. Lang. W. Lash Miller.
W. H. Ellis. *William Ramsay.*

W. B. Tuck.

Green, John Wilberforce,

22, Alwyne Road, Wimbledon.

Science Teacher. Student under R. Meldola. Assistant to C. E. Cassal, F.I.C. Works Chemist at National Explosives Co. and at Kynoch's, Ltd. Science Master at King's College School, Wimbledon Common, for last six years (appointed by Council of King's College, London).

W. J. Atkinson Butterfield. A. T. Cocking.
Bertram Blount. *Harold G. Colman.*

J. H. Coste.

Gwyer, Alfred George Cooper,

Keate House, Durdham Down, Bristol.

Chemist. B.Sc. (London); Ph.D. (Göttingen). 1905–7, 1851 Exhibition Science Research Scholar, Univ. Coll., Bristol. "On the Comparison of the Platinum Scale of Temperature with the Normal Scale at Temperatures between 444° and −190° C.," with Morris W. Travers, *Proc. Roy. Soc.*, **74** (1905), p. 528. "Über Al-Bi und Al-Sn

Legierungen," *Zs.f. anorg. Chem.*, **49** (1906), 311. "Über die Legierungen des Aluminiums mit Cu, Fe, Ni, Co, Pb, und Cd," *Zs.f. anorg. Chem.*, **57**, (1908), 113.

William Ramsay. J. C. Cain.
Edward C. Cyril Baly. H. E. Watson.
R. W. Gray.

Harland, Robert Main,

296, Willesden Lane, Willesden Green, N.W.

Analytical Chemist and Assayer. In practice as Analytical Chemist and Assayer, under style of Harland & Brown, of 37, Lombard Street, E.C.

C. T. Kingzett. B. E. R. Newlands.
R. C. Woodcock. *Samuel Rideal.*
W. R. Hodgkinson.

Haworth, Walter Norman, M.Sc.,

Dacca House, Chorley, Lancs.

Schunck Research Assistant in the Chemical Laboratories of the University of Manchester. Joint author of the following papers in the *Journal* of the Chemical Society: "Synthesis of Terpins, Terpineols, and Terpenes derived from Methyl*iso*propyl*cyclo*pentanes" (with Prof. W. H. Perkin), *Trans.*, 1908, **93**, **573**; also "Experiments on the Synthesis of 1-Methyl*cyclo*hexylidene-4-acetic Acid. Part II." (with V. J. Harding and Prof. W. H. Perkin), *Trans.*, 1908, **93**.

Harold B. Dixon. J. F. Thorpe.
W. H. Perkin. G. H. Bailey.
Norman Smith.

Hayward, Eric,

c/o W. R. Criper, Esq., Konnagar House, Konnagar, near Calcutta.

Manufacturing and Analytical Chemist (of D. Waldie & Co., Calcutta). Student at Finsbury Technical College, 1904 to 1907. King's College, London, 1907 and 1908. Passed the examination for A.I.C.

John M. Thomson. Henry R. Lyell.
Herbert Jackson. Alf. Chaston Chapman.
Patrick H. Kirkaldy. F. Guy Stirling Baker.

Higson, Frank,

Ivy Bank, Castle Street, Haulgh, Bolton, Lancashire.

Analytical Chemist. Assistant to Dr. Wagstaffe, M.Sc., F.I.C., Analytical and Consulting Chemist, Manchester.

R. L. Taylor. Stanley J. Peachey.
T. M. Nightingale. *James Ashton.*

C. A. Fogg.

Hoseason, James Henry,

Alderside, Timperley, Cheshire.

Manufacturing Chemist. Partner and Works Manager, Hough, Hoseason & Co., Manchester. Pharmaceutical Chemist. Six years Lecturer in Pharmacy, Materia Medica, and Pharm. Chemistry, Owens College, Victoria University, Manchester. Published various papers and notes of Pharmaceutical interest from the year 1889 on.

W. H. Perkin. F. Stanley Kipping.
G. H. Bailey. Francis J. H. Coutts.
J. F. Thorpe. Wm. B. Cowie.
Gilbert J. Fowler. Gerald Pinchbeck.

B. Prentice.

Hough, Ralph,

14, Longford Place, Victoria Park, Manchester.

Manufacturing Chemist. Chemist and Druggist. Partner and Manager of Messrs. Hough, Hoseason & Co., Manchester.

Francis J. H. Coutts. Gerald Pinchbeck.
Wm. B. Cowie. *Gilbert J. Fowler.*

B. Prentice.

Jackson, Robert Ernest,

York Villa, Shepherds Lane, Dartford.

Chemist in Factory (Wellcome Chemical Factory). Engaged in manufacture of medicinal chemicals, and desiring to keep in touch with modern progress in chemistry.

H. A. D. Jowett. Frederic H. Lees.
William C. Reynolds. Francis H. Carr.

Frank Lee Pyman.

Jeffery, John Hugh,

10, Daysbrook Road, Streatham Hill, London, S.W.

Analytical Chemist. Student in Chemical Department, King's College, London, during the Sessions 1905–8. Now Assistant to Mr. G. Cecil Jones, F.I.C.

John M. Thomson. Patrick H. Kirkaldy.
G. Cecil Jones. Henry R. Lyell.
Herbert Jackson. Tom R. Greenough.

Jones, Henry Humphreys,

18, Colquitt Street, Liverpool.

Teacher of Chemistry and Pharmacy at the Liverpool School of Pharmacy. Pharmaceutical Chemist.

A. C. Abraham. J. H. Allan.
J. W. Clayton. Prosper H. Marsden.
A. W. Titherley.

Keeble, Horace,

Wereham, Stoke Ferry, Norfolk.

Technical Chemist. Had experience in Sulphate of Ammonia Works; now engaged at Sulphate of Ammonia Works (Destructive Distillation of Peat) at Wereham, Norfolk. Recently (extending over six months) conducted chemical research on peat in the laboratory of William Elborne, Esq., M.A., Public Analyst and Official Agricultural Analyst for Peterborough.

F. W. Branson. Robert Wright.
J. H. Gough. *B. A. Burrell.*
William Kirkby. *Thomas Fairley.*

Leedham, Joseph,

176, Bromford Lane, West Bromwich.

Analytical Chemist. Chemist to Messrs. Willingsworth Iron Co., Incorp. (1908), Ltd., Wednesbury. Four years (articled) to Mr. J. Lones, F.I.C., Analyst to County Borough of Smethwick.

Arthur Adams. F. H. Alcock.
R. Lloyd Whiteley. *Harry Silvester.*
E. W. T. Jones.

McGillvray, John Esson,

15, Regent Street, Hartlepool.

Science Master. M.A. Degree (Edin.); 1st Class in Theor. and Practical Chemistry; Inter. B.Sc. (Lond.); 4 years Science Master, Pupil Teachers' Centre; Certificate classes, etc.

Alex. Crum Brown. J. Archyll Jones.
J. W. Patterson. *Geo. Fredk. Phillips.*
W. H. Jackson.

Martin, William George, B.Sc. (Wales),

Royal School, Armagh.

Schoolmaster (Chemistry and Physics). Three years senior Science Master, Sandymount Presbyterian College, Dublin. Associate of

Univ. College of S. Wales and Monmouthshire; B.Sc. (Wales). For 4 years Monmouthshire C.C. Technical Scholar.

W. H. Cadman. H. M. Atkinson.
A. O'Farrelly. Geo. A. Watson.
James H. Pollok.

May, Percy,
126, Cazenove Road, Stamford Hill, N.

Research Student and Demonstrator in Chemistry at University College, London. Research Student and Demonstrator; Tuffnell Scholar, etc., University College, London.

William Ramsay. R. W. Gray.
H. E. Watson. A. W. Stewart.
Samuel Smiles. N. T. M. Wilsmore.

Morley, William Norton,
325, Brownhill Road, Catford, S.E.

Chemistry Student; after Jan., 1909, Schoolmaster. 2nd Class Honours Chemistry at B.Sc., 1908. Research Student and Demonstrator in Chemistry at University College, London; just appointed an assistant master at Colfe's Grammar School, Lewisham, and wish to keep in touch with the advance of Chemistry.

William Ramsay. Edward C. Cyril Baly.
J. Norman Collie. Samuel Smiles.
E. de Barry Barnett.

Painter, Frederick Hubert, B.Sc. (Lond.),
Heatherbank, Alum Chine Road, Bournemouth.

Teacher of Chemistry and Physics. Head Science Master and Lecturer in Chemistry and Physics at the Bournemouth Schools of Science and Art from Sept., 1896, to the present time. For several years previous to 1896 was engaged in private tuition in Chemistry.

Arthur P. Luff. *G. E. Scott-Smith.*
Fredk. Hudson-Cox. *John Evans.*
John G. Howarth. *S. Ernest Melling.*
George Brownen. *Wm. H. Simmons.*

Pickard, Joseph Allen,
3, West Kensington Terrace, W.

Asst. Demonstrator in Chemistry at the Royal College of Science. Associate of the Royal College of Science, London (in Chemistry). B.Sc. London (Chemistry).

William A. Tilden. James C. Philip.
G. T. Morgan. W. Godden.
M. O. Forster.

Pope, Frank Geo.,

28, Alcester Crescent, Upper Clapton, London, N.E.

Assistant Lecturer, East London College (Chem. Dept.). Whole or part author of papers, *Transactions*, 1896 (1265); 1897 (1084); 1898 (174); 1901 (1146); 1908 (532). *Berichte*, 1896 (2824); 1897 (1624).

J. T. Hewitt. Edward C. Cyril Baly.
Clarence Smith. John Wade.

M. O Forster.

Regan, Colston James,

"Nestleton," 14, Penerley Road, Catford, S.E.

Student at University College, London. Inter. B.Sc. (London), 1906. Working in Laboratory at Univ. Coll. for two and a half years.

J. Norman Collie. N. T. M. Wilsmore.
William Ramsay. Samuel Smiles.
R. W. Gray. Charles M. Stuart.

Robinson, Robert, M.Sc.,

Field House, Chesterfield.

Research Student in Organic Chemistry, Manchester University (1851 Exhibition Scholar, 1906). Joint Author with Professor W. H. Perkin, F.R.S., of several papers in the *Proceedings*, and of the following memoirs in the *Transactions*: "Brazilin and Hæmatoxylin. VII." (*Transactions* of the Chemical Society, **91**, 1073—1103); "Brazilin and Hæmatoxylin. VIII." (*Transactions* of the Chemical Society, **93**, 489—517); "Brazilin and Hæmatoxylin. IX." (*Transactions* of the Chemical Society, **93**, 1115—1162, with Dr. Paul Engels); "The Synthesis and Constitution of Certain Pyranol Salts related to Brazilein and Hæmatein" (*Transactions* of the Chemical Society, **93**, 1085—1115, with M. R. Turner).

Harold B. Dixon. G. H. Bailey.
W. H. Perkin. J. F. Thorpe.

Norman Smith.

Rogers, Herbert,

Stenning House, Cobwell Road, Retford, Notts.

Works Chemist. Received training in Chemistry at East London, West Ham, and East Ham Technical Colleges. Five year Assistant

Chemist to Western Electric Co., North Woolwich, and for two years past Chemist to the Northern Rubber Co., Retford, Notts.

Francis Martin. *Wesley Lambert.*
H. H. Ashdown. *A. H. Mundey.*
A. E. Dunstan. *H. Heron Smith.*
C. Schlienger. *R. L. Smith.*

Sageman, Philip John,

160, Brecknock Road, London, N.

Analyst, Government Laboratory. Seven years' experience in Government Laboratory under Dr. Thorpe, F.R.S., and Mr. E. Grant Hooper, F.I.C. Contribution (*Trans. Chem. Soc.*, 1907): "Molecular Aggregation in Solution, etc." (Holmes and Sageman).

T. E. Thorpe. M. O. Forster.
E. Grant Hooper. James C. Philip.
William A. Tilden. G. T. Morgan.

Schulten, J. H. Charles,

4, Pollock Street, Calcutta.

Proprietor of Analytical and Consulting Laboratory. Doctor Philosophiae, Erlangen, 1895. Dissertation: "Beiträge zur Kenntnis fester Lösungen"; "Manures: Their Action, Composition, and Use," *Gardening and Planting*, 1902; "Soil Analysis," *Planters' Gazette*, 1903; "New Method of Detecting Rosin in Shellac" (not yet published); in preparation: "The Use of Manures."

Paul Brühl. W. H. Arden Wood.
David Hooper. E. Sommerfeldt.
William Tate.

Segaller, David,

69, Dover Road, Wanstead Park, E.

Science Master, East Ham Technical College. A.R.C.S. (Dublin). Works Chemist of Mercerising Company, Macclesfield. Then Chemistry Master, Blackburn Grammar School. Now Science Master, East Ham Technical College. Studied with Prof. Lunge at Zurich.

W. N. Hartley. W. H. Perkin.
G. Lunge. W. H. Barker.
W. J. Pope. A. E. Dunstan.

Stevenson, James Thomas,

67, Surrey Street, Sheffield.

Partner in the firm of A. H. Allen & Partners, Analytical Chemists.

G. E. Scott-Smith. S. Ernest Melling.
John Evans. Otto Hehner.

J. Carter Bell.

Varley, Reginald Wells,

Glenroy, 12, Mill Hill Road, Derby.

Analytical Chemist. Fourteen years Analytical Chemist to the Leeds Forge Co., 2½ years Chief Chemist to the Monkbridge Iron Co., 2 years Chief Chemist to the Fitzwilliam Hemsworth Co., 6 months Chief Chemist to the Clay Cross Co., and then engaged by Sir Francis Ley, Bart., as Chief Chemist to Ley's Malleable Castings Co., Vulcan Ironworks, Derby; sometime Lecturer in Metallurgy.

Harry W. Dixon. B. A. Burrell.
Harry J. Unwin. Herbert Eccles.

Arthur W. Cooke.

Warwick, Guy Ransom,

5 and 6, Fowkes Buildings, Great Tower Street, London, E.C.

Consulting and Analytical Chemist, especially as applied to Brewing, Distilling, and Malting. B.A. degree Cambridge, Natural Science Tripos; subjects: Chemistry, Physics, Botany, and Geology. Joint author of research on "The Influence of Light and Spectral Colours on the Sporulation and Vitality of Yeast."

Horace T. Brown. M. M. Pattison Muir.
J. E. Purvis. A. Hutchinson.

C. T. Heycock.

West, Percy Charles Henry,

40, The Green, Norton, Co. Durham.

Analytical Chemist. For three years a student in the laboratories of University College, London, during part of which period engaged in research; now and for the past five years engaged as works chemist. Contributor to technical journals.

J. Norman Collie. N. T. M. Wilsmore.
William Ramsay. Samuel Smiles.

A. W. Stewart.

Wild, Thomas Jabez,

Scott's Laboratories, Southall, Middlesex.

Pharmaceutical Chemist, Analyst, Member of the Pharmaceutical Society. For 2 years student at the Pharmaceutical Society's School

(1898–1899); passed Minor and Major examinations. Attended lectures on Chemistry, and studied Practical Chemistry at above School under Professor Collie. For 2 years in Hong Kong, Assistant Government Analyst under Mr. Frank Browne, F.C.S. For 1 year in Hong Kong, Acting Government Analyst (1899–1902). For 5½ years Analytical Chemist to Messrs. Scott & Browne, Ltd., Southall (May, 1903, to present date).

Frank Browne. William Forster.
J. Norman Collie. Horace Finnemore.
Arthur Lapworth.

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Issued 27/2/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 352.

Thursday, February 18th, 1909, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society in consequence of the death of three Honorary and Foreign Members, Professor Wolcott Gibbs (elected May 3rd, 1866: deceased, Dec. 9th, 1908), Professor Emil Erlenmeyer (elected Feb. 1st, 1883: deceased, Jan., 22nd, 1909), and Professor Julius Thomsen, F.R.S. (elected May 18th, 1876: deceased, Feb. 13th, 1909). The death of Professor W. H. Hudleston, F.R.S., was also announced.

The PRESIDENT stated that the Council had recommended Professor Dr. Georg Lunge as an Honorary and Foreign Member, and that his election would be balloted for at the next Ordinary Scientific Meeting of the Society. Fellows wishing to participate in the forthcoming Celebration of Professor Lunge's 70th birthday on Sept. 15th., 1909, should forward their subscriptions to Professor E. Bosshard, Eidgenössisches Chemiegebäude, Zürich.

Messrs. D. Avery, W. C. Birch, H. Green, and H. Main were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Hugh Garner Bennett, M.Sc., 13, Spring Grove Terrace, Leeds.
Frank Playfair Burt, B.Sc., Elmhyrst, Weston-super-Mare.

Reginald Cyril Herbert Cooke, 17, St. Edmund's Terrace, Regent's Park, N.W.

Henry Jermain Maude Creighton, M.A., Halifax, Nova Scotia, Canada.

Philip Henry Crewe, Glencairn, Woods Moor, Stockport.

John Frederick Haws, Parkfield Villa, Newton-by-Frankby, Cheshire.

Reginald Vernon Hickinbotham, 144, West Street, Maritzburg, Natal.

Arthur Edwin Tate, B.Sc., Gladstone House, Salter Row, Pontefract.

Francis Lawry Usher, B.Sc., 18, Clifton Park, Bristol.

The selection by the Council of Professor F. S. Kipping, F.R.S., as Longstaff Medallist for 1909 was announced, the presentation to be made at the Annual General Meeting.

It was stated that the following changes in the Officers and Council were proposed by the Council:

President to retire: Sir William Ramsay, K.C.B.

Vice-Presidents to retire: Dr. R. Messel and Prof. W. H. Perkin.

Ordinary Members of Council to retire: Dr. H. A. D. Jowett, Dr. F. E. Matthews, Dr. W. J. Sell, Dr. J. Wade.

As President: Prof. Harold B. Dixon.

As Vice-Presidents who have filled the office of President: Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Sir William Ramsay, Prof. J. Emerson Reynolds, Sir Henry E. Roscoe, Dr. W. J. Russell, Prof. T. E. Thorpe, and Prof. W. A. Tilden.

As Treasurer: Dr. Alexander Scott.

As Hon. Secretaries: Dr. M. O. Forster and Prof. Arthur W. Crossley.

As Foreign Secretary: Dr. Horace T. Brown.

As Vice-Presidents: Prof. J. Campbell Brown, Prof. J. N. Collie, Dr. J. J. Dobbie, Prof. F. S. Kipping, Sir A. Pedler, Prof. James Walker.

As New Ordinary Members of Council: Prof. W. A. Bone, Mr. C. E. Groves, Dr. G. T. Morgan, Dr. A. E. H. Tutton.

Dr. Arthur Harden, Dr. V. H. Veley, and Dr. J. A. Voelcker were elected Auditors to Audit the Society's Accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared elected:

George Henry Joseph Adlam, B.A.
Hubert Brunskill.
Arthur Clayton, B.Sc.
Herbert Edwin Cocksedge, B.A., B.Sc.
Alfred Bertram Coles, M.A.
John Charles Jesser Coope.
Frederick Percy Dunn, B.Sc.
Frederick Ferraboschi.
John Thomas Fox.
Arthur Gordon Francis, B.Sc.
John Thomas Furnell.
Ross Aiken Gortner, M.A., B.Sc.
John Wilberforce Green.
Alfred George Cooper Gwyer, B.Sc., Ph.D.
Robert Main Harland.
Walter Norman Haworth, M.Sc.
Eric Hayward.
Frank Higson.
James Henry Hoseason.
Ralph Hough.
Robert Ernest Jackson.
John Hugh Jeffery.
Henry Humphreys Jones.
Horace Keeble.
Joseph Leedham.
John Esson McGillvray, M.A.
William George Martin, B.Sc.
Percy May.
William Norton Morley, B.Sc.
Frederick Hubert Painter, B.Sc.
Joseph Allen Pickard, B.Sc.
Frank George Pope.
Colston James Regan.
Robert Robinson, M.Sc.
Herbert Rogers.
Philip John Sageman.
J. H. Charles Schulten, Ph.D.
David Segaller.
James Thomas Stevenson.
Reginald Wells Varley.
Guy Ransom Warwick, B.A.
Percy Charles Henry West.
Thomas Jabez Wild.

Of the following papers, those marked * were read:

*45. "A study of some asymmetric compounds." By Frederic Stanley Kipping.

When a *dl*-acid is treated with a *d*-base, the product is a mixture of the *d*A*d*B- and *l*A*d*B-salts, and when a *d*-acid is combined with a *dl*-base, the components of the product are *d*A*d*B and *d*A*l*B. If therefore A and B represent a particular acid and a particular base respectively, and *dl*-A may be resolved with the aid of *d*-B, it might be inferred that *dl*-B could also be resolved with the aid of *d*-A. The *d*A*d*B-component is common to both original products, and as *l*A*d*B and *d*A*l*B are enantiomorphously related and have the same solubility in any given optically inactive solvent, the observed difference in solubility between *d*A*d*B and *l*A*d*B should also be effective in the case of *d*A*d*B and *d*A*l*B.

Now *dl*-sulphobenzylethylpropylsilicyl oxide may be resolved with *d*- (or with *l*-)methylhydrindamine (Trans., 1908, **93**, 457); experiments showed, however, that *dl*-methylhydrindamine could not be resolved with the aid of *d*-sulphobenzylethylpropylsilicyl oxide under similar conditions.

dl-Methylhydrindamine may be resolved by fractionally crystallising its *d*-hydrogen tartrate from water (Tattersall, Trans., 1904, **85**,

169); it is now shown that *dl*-tartaric acid may be resolved with *d*-methylhydrindamine under similar conditions, and that both the *d*A*d*B- and the *l*A*d*B-components may be isolated in one series of crystallisations.

dl-Hydrindamine cannot be resolved by fractionally crystallising its *d*-mandelate from water; *dl*-mandelic acid, however, is very easily resolved by fractionally crystallising from water its salt with *d*-(or with *l*-)hydrindamine.

These results seem to show that partly racemic molecules exist in solution.

Discussion.

Mr. A. E. Dunstan agreed with Prof. Kipping that the physico-chemical evidence for the existence of racemic compounds in solution was slight, owing to the dissociation of these substances, but he pointed out that the results published by Clerk Ranken and Taylor, Stewart, Dunstan and Thole, all indicated that undoubtedly there was a small difference between the physical properties of the racemic and the active compound when dissolved. Moreover, these differences were consistent and increased with the concentration.

***46. "The decomposition and sublimation of ammonium nitrite." By Prafulla Chandra Rây.**

When an aqueous solution of ammonium nitrite is heated in a vacuum at about 37—40°, only a very small portion of the salt decomposes according to the equation: $NH_4NO_2 = 2H_2O + N_2$; the main bulk of the salt crystallising out. If the temperature is then gradually raised to 70°, slow decomposition continually proceeds according to the above equation, but the major portion sublimes unchanged. When this sublimate is heated by means of a naked flame, the gaseous products are nitrogen and nitric oxide, the latter often amounting to as much as 6 per cent.

Discussion.

Dr. Divers remarked on the interest attached to the crystallisation of ammonium nitrite from its aqueous solution and of the sublimation of a salt hitherto supposed to be too unstable for these operations to be possible. The generation of much nitric oxide when the sublimed salt was vaporised and further heated seemed to indicate the occurrence of a decomposition tending to that production of hydrazine which Professor Rây had looked for: $2NH_4NO_2 = N_2H_4 + 2H_2O + 2NO$, the elements of the hydrazine appearing as ammonia and nitrogen.

Dr. VELEY concurred with the author that ammonium nitrite in solution is best prepared by the decomposition of silver nitrite and ammonium chloride. It was a most interesting point that such a solution could be evaporated in a vacuum without decomposition, and that the ammonium nitrite could not only be crystallised out, but even purified by sublimation.

The observation was remarkable that if the conditions were such that the solid salt decomposed, then nitric oxide in a small proportion was formed in addition to nitrogen. Blanchard (*Zeitsch. physikal. Chem.*, 1902, **41**, 681; and *ibid.*, 1905, **51**, 117) had shown that when an aqueous solution containing potential ammonium nitrite is heated under atmospheric pressure, nitric oxide is formed in about the same proportion as that found by the author, but on reduction of pressure the proportion is reduced to *nil*. It would thus appear that the solid salt and aqueous solutions give the same result, although under reverse conditions.

***47. "The estimation of hydroxyl derivatives in mixtures of organic compounds." By Harold Hibbert.**

Hibbert and Sudborough's method (Trans., 1904, **85**, 933) for the estimation of hydroxyl groups in carbon compounds can be applied with equal success to mixtures of hydroxyl derivatives with other organic compounds, for example, ketones, esters, nitriles, etc. It is necessary to take rather more of the Grignard reagent than is sufficient to combine with both substances.

In this way the author has been able to estimate α-naphthol in presence of various ketones, ethyl benzoate, methyl hydrogen succinate, and acetonitrile, as well as chloral in a mixture of this with acetone.

***48. "A simple method for determining the chemical affinity* of organic substances." By Harold Hibbert.**

The author has shown (preceding paper) that hydroxyl derivatives can be estimated in presence of ketones if excess of the Grignard reagent is employed. If now a quantity of the latter is taken, insufficient to combine with both, it is obvious that a partition

* The author suggests using the term *affinergy* (compounded from *affin*-ity and en-*ergy*; German equivalent = affinergie) as a substitute for Michael's *chemical potential* (*Annalen*, 1908, **363**, 21) in order to avoid confusion with the physical conception of potential (as in electrical potential), with which it has nothing in common.

of the reagent between the two substances will take place, and the amount of methane evolved will depend on their relative masses and reaction velocities, assuming, of course, that all the products (apart from the methane) remain in solution. The latter condition is fulfilled by working in phenetole solution. By taking the same hydroxyl compound, mixing it with equimolecular quantities of various ketones, and using the same (insufficient) amount of magnesium methyl iodide solution, it is thus possible to measure the relative reaction velocities of the ketones towards the reagent, since these are indirectly proportional to the amounts of methane evolved. The method serves in this way as a means for determining the chemical affinity of organic compounds.

The relative affinities (using α-naphthol) of the following ketones have already been determined: dimethyl, methyl ethyl, and diethyl ketone; aceto- and benzo-phenone.

Discussion.

Dr. Lapworth asked if the author had fully considered his assumption that velocity of reaction in non-reversible changes might be taken as a measure of affinity. Scientists were agreed that changes could only occur spontaneously when a diminution in potential thereby resulted, but at present this principle, whilst often serving to indicate the direction of change in a chemical system, was difficult to develop for irreversible changes, and the determination of affinity seemed hardly satisfactory except in such cases where equilibrium conditions could be ascertained.

Dr. Senter said that in his opinion the reactivity of a chemical system could best be expressed, with van't Hoff, by means of the equation:

$$\text{Reaction Velocity} = \text{Driving Force}/\text{Resistance}.$$

The driving force was the "chemical affinity" and depended on the free energy of the system, which could be calculated, in a perfectly definite way, from equilibrium measurements. The reaction velocity might be enormously affected by slight changes in the medium or by catalysts, neither of which could, in general, modify to any great extent the free energy (or the chemical affinity). The fact that the free energy and the reaction velocity are affected so differently by reagents allowed to some extent of their investigation separately, and therefore this method of regarding the matter seemed to possess distinct advantages.

The President remarked that it is essential to distinguish between an energy and one of the factors of an energy:

just as Heat Energy = Temperature × Entropy,
and as Electric Energy = Electric potential × Electric quantity,
so Chemical Energy = Chemical Affinity × Chemical quantity.

Now as chemical quantity is proportional to electric quantity (as is proved by Faraday's law), it follows that chemical and electric affinity must also be proportional. Therefore, by determining electric potential, chemical affinity is measured.

The word "affinergy" appears to be confusing, inasmuch as it combines the conception of a factor of an energy with the energy itself.

***49. "Chlorine generated by potassium permanganate: its preparation and purity." By Edgar Wedekind and Samuel Judd Lewis.**

The method of preparing chlorine by dropping concentrated hydrochloric acid on crystals of potassium permanganate, which was suggested by Graebe (*Ber.*, 1902, **35**, 43), is stated to yield the gas free from oxides of chlorine, but no experimental proof of this is given by that author.

The purity of the gas has now, however, been ascertained by the following experiments: (1) On passing the gas through sulphuric acid no reddish coloration is produced, showing the absence of chlorine peroxide. (The formation of chlorine monoxide is improbable, as this would be at once decomposed by the hydrochloric acid.) (2) 2·11 Grams of tin were heated to dull redness in a stream of the gas; the residue weighed only 0·7 milligram. (3) The gas is completely absorbed by mercury. (4) A definite volume of the gas was absorbed by a solution of 15 grams of potassium iodide in water, and the iodine liberated was titrated with sodium thiosulphate solution, of which 168·70 c.c. (mean of four determinations) were required, whereas in a corresponding experiment with chlorine, generated from pure manganese dioxide and hydrochloric acid (and assumed to be free from oxides of chlorine, carbon dioxide, etc.), 168·67 c.c. of thiosulphate solution (mean of six determinations) were used.

Discussion.

Dr. Scott pointed out that, as potassium permanganate often contains small quantities of chlorate, chlorine prepared by its means is peculiarly liable to be contaminated with traces of chlorine oxides. The only safe test for the presence of these is to absorb the gas in a neutral solution of potassium iodide, and then decolorise it

exactly by means of sodium thiosulphate; if, on adding to the colourless solution pure dilute hydrochloric acid, no iodine is liberated, then the chlorine may be regarded as quite free from its oxides, but any iodine liberated is exactly equivalent to the combined oxygen, since, in neutral solution, it goes to form iodate in accordance with the following equations:

$$3Cl_2O + 7KI = 3I_2 + KIO_3 + 6KCl \qquad 3Cl_2 = 3I_2$$
$$3Cl_2O + 12KI + 6HCl = 6I_2 + 3H_2O + 12KCl \qquad 3(O) = 3I_2$$

and

$$6ClO_2 + 10KI = 3I_2 + 4KIO_3 + 6KCl \qquad 3Cl_2 = 3I_2$$
$$6ClO_2 + 30KI + 24HCl = 15I_2 + 12H_2O + 30KCl \qquad 6O_2 = 12I_2.$$

Neither of the authors' assumptions: (*a*) that hypochlorous anhydride must be absent, because of the presence of a large excess of hydrochloric acid, or (*b*) that chlorine peroxide could not be present, as the sulphuric acid by which the gas was dried did not acquire a reddish colour, was justified. What their experiments did prove was that the gas thus prepared was of the same order of purity as that from hydrochloric acid and manganese dioxide.

50. "The isolation of the aromatic sulphinic acids." By John Thomas.

The aromatic sulphinic acids are characterised, as a class, by forming ferric salts which are insoluble in water and fairly concentrated mineral acids; this property can be usefully applied in the separation of these acids from the solutions in which they are produced. The ferric salts of benzenesulphinic, *o*- and *p*-toluenesulphinic, and α- and β-naphthalenesulphinic acids have been prepared and characterised, and simple methods indicated for converting them into the corresponding sulphinic acids, sulphonyl chlorides, and sulphonamides.

51. "Analytical investigation of zirconium metal." By Edgar Wedekind and Samuel Judd Lewis.

In view of zirconium having not yet been obtained in a pure condition, and of the lack of analytical data regarding the composition of the specimens obtained by various workers, the authors have worked out methods of analysis which make it possible to determine the proportions of the most common impurities. The zirconium existing in the free state is separated as the tetrachloride from that in combination with oxygen by burning the substance in pure chlorine; in this way the proportion of oxygen is determined directly. Nitrogen is

estimated by a method similar to that of Kjeldahl; carbon by combustion of the metal in oxygen at very low pressure, and subsequent absorption of the carbon dioxide produced.

52. **"The action of ethylene dibromide on monomethylaniline." By John Gunning Moore Dunlop and Humphrey Owen Jones.**

By the interaction of two gram-molecules of monomethylaniline with one gram-molecule of ethylene dibromide, diphenylpiperazine (m. p. 163°) is formed by a reaction represented by the equation:

$$4NHMePh + 2C_2H_4Br_2 = PhN\begin{<}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{>}NPh,2HBr + 2NMe_2Ph,HBr.$$

When four gram-molecules of monomethylaniline are used instead of two in this interaction, diphenyldimethylethylenediamine,

$$NMePh\cdot CH_2\cdot CH_2\cdot NMePh,$$

melting at 47°, is produced.

53. **"Salicylidene-*m*-toluidine, a new phototropic compound; salicylideneamines: salicylamides." By Alfred Senier and Frederick George Shepheard.**

In continuation of previous work on acridine synthesis, a series of new salicylideneamines and salicylamides have been prepared. Among these, *salicylidene*-m-*toluidine* has special interest, as it exhibits phototropy (Marckwald, *Zeitsch. physikal. Chem.*, 1899, **30**, 140). On crystallisation from its solutions, the crystals are pale yellow, but when exposed to sunlight the colour changes quickly to deep orange, and this colour change is reversed, although more slowly, when the crystals are placed in the dark. This reversible reaction is due to light waves of high refrangibility; it does not take place in solution, and the sensibility of the compound remains unimpaired after at least a month's time. No evidence could be obtained of triboluminescence or phosphorescence. Salicylidene-*m*-toluidine behaves in this respect like the anhydrous chloride of quinoquinoline and β-tetrachloro-α-ketonaphthalene studied by Marckwald. It is similar also to the fulgenic acid compounds investigated by Stobbe (*Annalen*, 1908, **359**, 1). Probably phototropy in this instance, as is supposed to be the case in others, depends on the existence of two stereo- or other isomerides formed respectively under the influence of short or long waves of light.

54. "The action of ethyl carbamate on esters of organic acids and mustard oils." By Siegfried Ruhemann and John Gillies Priestley.

Ethyl phenylpropiolate does not form an additive product with ethyl sodiocarbamate, but condenses with it to yield *ethyl phenylpropiolylcarbamate*, $C_6H_5C{:}C{\cdot}CO{\cdot}NH{\cdot}CO_2Et$. This reaction has been applied to the preparation of acyl derivatives of ethyl carbamate from esters of fatty and fatty-aromatic acids. In this way, also, *ethyl formylcarbamate*, $CHO{\cdot}NH{\cdot}CO_2Et$, has been obtained, which is readily hydrolysed by mineral acids, even in the cold.

The esters of benzenecarboxylic acids form either only very small quantities of the acyl derivatives of ethyl carbamate, as with ethyl benzoate, or no trace of the acyl carbamate, as with ethyl *o*-phthalate.

Phenylthiocarbimide reacts with ethyl sodiocarbamate to form carboxyethylphenylthiocarbimide, $NH(CO_2Et){\cdot}CS{\cdot}NH{\cdot}C_6H_5$ (see Doran, *Trans.*, 1896, **69**, 326), and a yellow compound having the formula $\begin{matrix} C_6H_5{\cdot}NH{\cdot}CS{\cdot}N\text{—}CO \\ C_6H_5{\cdot}N{:}C\text{—}S \end{matrix}$, which is *anhydro-diphenyldithiobiuret-carboxylic acid*. It forms colourless sodium and potassium salts, and is readily decomposed by alkalis. Allylthiocarbimide yields with ethyl sodiocarbamate a substance, $C_9H_{11}ON_3S_2$, with similar properties to those of the former compound.

55. "The hydrolysis of amygdalin by emulsin. Part III. Synthesis of *d*-benzaldehydecyanohydrin." By Samuel James Manson Auld.

The assumption generally made that benzaldehydecyanohydrin must be formed as an intermediate product of the decomposition of amygdalin by emulsin is objected to, and evidence has been brought forward showing that an asymmetric synthesis of *d*-benzaldehydecyanohydrin takes place under the influence of emulsin, and that its formation in this manner proceeds more rapidly than its formation during the hydrolysis of amygdalin by emulsin. Emulsin can also induce the formation of an optically active hydroxybenzaldehydecyanohydrin from hydroxybenzaldehyde and hydrocyanic acid.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Fischer, *Emil.* Untersuchungen über Kohlenhydrate und Fermente (1884—1908). pp. viii + 912. Berlin 1909. (*Recd.* 21/1/09.)
From the Author.

Guttmann, *Oscar.* The manufacture of explosives. Twenty years' progress. Four Cantor Lectures delivered at the Royal Society of Arts in November and December, 1908. pp. viii + 84. ill. London 1909. (*Recd.* 17/2/09.)
From the Publishers: Messrs. Whittaker & Co.

Gordon Memorial College, Khartoum. Third report of the Wellcome Research Laboratories. pp. 477. ill. London 1908. (*Recd.* 15/2/09.) From the Director.

—— Supplement to the third report. Review of some of the recent advances in tropical medicine. By *Andrew* **Balfour** and *R. G.* **Archibald.** pp. 251. London 1908. (*Recd.* 15/2/09.)
From the Director.

Johnson, *Charles Morris.* Rapid methods for the chemical analysis of special steels, steel-making alloys, and graphite. pp. vi + 221. New York 1909. (*Recd.* 12/2/09.)
From the Publishers: Messrs. John Wiley & Sons.

Linnean Society of London. The Darwin-Wallace Celebration held on Thursday, 1st July, 1908. pp. viii + 134. ill. London 1908. (*Recd.* 15/2/09.) From the Society.

Senter, *George.* Outlines of physical chemistry. pp. xvii + 369. ill. London 1909. (*Recd.* 26/1/09.)
From the Publishers: Messrs. Methuen & Co.

Stewart, *Alfred Walter.* Recent advances in organic chemistry. pp. xv + 296. London 1908. (*Recd.* 25/1/09.) From the Author.

Symons, *Brenton.* Genesis of metallic ores and of the rocks which enclose them. pp. xxxiii + 494. ill. London 1908. (*Recd.* 19/1/09.)
From the Author.

Woburn Experimental Fruit Farm. Tenth report. By the **Duke of Bedford** and *Spencer U.* **Pickering.** pp. iv + 50. London 1909. (*Recd.* 26/1/09.) From the Authors.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Metropole, at 6.30 for 7 o'clock, on Thursday, March 25th, 1909 (the day fixed for the Annual General Meeting).

The price of the tickets will be One Guinea each, including wine.

All applications for tickets must be received not later than Thursday, March 18th next.

Tickets will be forwarded to Fellows on receipt of a remittance for the number required, made payable to "Mr. S. E. Carr" and addressed to the Assistant Secretary, Chemical Society, Burlington House, W.

At the next Ordinary Scientific Meeting, on **Thursday, March 4th, 1909**, there will be a ballot for the election of an Honorary and Foreign Member, and the following papers will be communicated :

"The action of anhydrosulphuric acid on triphenylsilicol." By G. Martin and F. S. Kipping.

"The ignition temperatures of gases." By H. B. Dixon and H. F. Coward.

"Diazohydroxylamino-compounds and the influence of substituting groups on the stability of their molecules." By N. L. Gebhard and H. B. Thompson.

"Tetraketopiperazine. Part II." By A. T. de Moulpied and A. Rule.

"The alkaloids of *Senecio latifolius*." By H. E. Watt.

"The miscibility of the pyridine bases with water and the influence of a critical-solution point on the shape of the melting-point curve." By O. Flaschner.

"An interpretation of the Hantzsch-Werner hypothesis." By M. O. Forster and F. P. Dunn.

"The triazo-group. Part IX. Transformation of cinnamoylazoimide into cinnamenylcarbimide (cinnamenyl *iso*cyanate)." By M. O. Forster.

"The preparation of dichlorocarbamide." By F. D. Chattaway.

"The interaction of methylenediamines or methyleneanilines and carbimides or thiocarbimides; thiotetrahydroquinazolines, methylenecarbamides, dicarbanilidomethylenediamines and their homologues." By A. Senier and F. G. Shepheard.

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Issued 12/3/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 353.

Thursday, March 4th, 1909, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. A. G. C. Gwyer, R. E. Jackson, G. T. Morgan, W. N. Morley, C. S. Mummery, C. J. Regan, M. S. Salamon, and A. W. Stewart were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Harry Livsey, 54, Pemberton Street, Old Trafford, Manchester.
Robert Cecil Owen, B.Sc., 89, Foregate Street, Chester.
Norman Scott Rudolf, M.Sc., Bangalore, India.
Henry Llewellyn Smith, B.Sc., 23, Ellingham Road, Shepherd's Bush, W.
Arthur Percy Strohmenger, Bridgebank, Harrow-on-the-Hill.
George Bilderbeck Walker, Vale House, Trafalgar Road, Greenwich, S.E.

Dr. DIVERS gave notice that, at the Annual General Meeting of the Society on March 25th next, he would move the adoption of a new Bye-law, to run as follows:

XIII *bis.*—*On Ascertaining the Will of the Society by means of Voting Papers.*

The President, either on his own motion or on a written requisition by the Council or by fifty Fellows, shall proceed to ascertain the will

of the Society as to any suggested change in the Bye-laws or in the administration of these laws by the Council, by causing to be delivered, along with the Proceedings or separately, a notice to each Fellow of the change proposed, together with a voting paper upon it, to be filled in by the Fellow and returned to the Secretaries not later than a prescribed date. After that date, the results of the voting shall be counted by the Secretaries and two Scrutineers, appointed by the President, and be reported by him to a Council Meeting and to a General Meeting, upon which the Council shall proceed to act in accordance with the majority of votes, as being the expression of the will of the majority.

The PRESIDENT read the names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council of the Society.

A Ballot for the election of an Honorary and Foreign Member was held, and the PRESIDENT declared subsequently that Prof. Dr. Georg Lunge, of Zürich, had been unanimously elected.

Of the following papers, those marked * were read:

***56. "The action of fuming sulphuric acid on triphenylsilicol." By Geoffrey Martin and Frederic Stanley Kipping.**

Tetraphenylsilicane is decomposed by fuming sulphuric acid, giving sulphonic derivatives of benzene (Kipping and Lloyd, *Trans.*, 1901, **79**, 449), and phenylbenzylethylpropylsilicane is decomposed by sulphuric acid, the phenyl group being eliminated in the form of benzene (Kipping, *Trans.*, 1907, **91**, 209).

These facts led the authors to doubt the existence of the "triphenylsilicoltrisulphonic acid" recently described by Ladenburg (*Ber.*, 1907, **40**, 2274; 1908, **41**, 966), and a repetition of his experiments leads to the conclusion that his acid is not only a mixture, but also that it does not contain any appreciable quantity of triphenylsilicoltrisulphonic acid.

Even when triphenylsilicol is treated with fuming sulphuric acid at $-10°$, the greater part, if not the whole, of the silicol is decomposed and benzenesulphonic acid is formed, whereas at higher temperatures benzenedisulphonic acid is produced; no compound containing silicon was isolated, but evidence pointing to the presence of diphenylsiliconedisulphonic acid, $SiO(C_6H_4 \cdot SO_3H)_2$, in the crude product was obtained.

l-*Menthylamine benzenesulphonate*, $C_6H_5 \cdot SO_3H, C_{10}H_{21}N$, forms colourless needles, melts at 223—226°, and is readily soluble in water, alcohol, or chloroform, but sparingly soluble in ethyl acetate.

l-*Menthylamine benzenedisulphonate*, $C_6H_4(SO_3H)_2,(C_{10}H_{21}N)_2$, melts at 212°, and is readily soluble in ethyl acetate, alcohol, or water, but insoluble, or nearly so, in ether.

*57. "The ignition-temperatures of gases."
By Harold Baily Dixon and Hubert Frank Coward.

The temperature to which two gases must be heated in order that, when brought into contact, they will inflame immediately has been determined by passing an inflammable gas up a tube, terminating in a nozzle, fixed in the centre of a second tube conveying a current of air or oxygen, and electrically heated. Thus no reaction occurred during the preliminary heating of the gases. The temperature of the gas 2 mm. below the nozzle was measured by means of a protected thermo-junction.

The ignition-temperature of hydrogen thus obtained was constant, within 10°, under variation of the following circumstances:

(1) The rates of flow of the gases, within wide limits.

(2) The size, material, and surface condition of the jet and of the walls of the furnace.

(3) The rate of heating of the furnace.

(4) The position of the thermo-junction, either inside or just outside the nozzle.

The ignition-temperature was at first decreased some 20° by increasing the diameter of the outer tube, but a limit was then reached when doubling the diameter produced no further decrease.

The ignition-temperature was raised 5° by working under half an atmosphere pressure, but decreased by 30° under a pressure of two atmospheres.

The ignition-temperature of hydrogen in air is the same as in oxygen.

The results obtained at atmospheric pressure are given in the following table. The paraffins and ammonia gave numbers varying

	Ignition-temperature			
	in oxygen.		in air.	
Gas.	Between.	Mean.	Between.	Mean.
Hydrogen	580—590°	585°	580—590°	585°
Carbon monoxide (moist)	637—658	650	644—658	651
Cyanogen	803—818	811	—	—
Ethylene	500—519	510	542—547	543
Acetylene	400—440	428 (?)	406—440	429
Hydrogen sulphide	220—235	227	346—379	364
Methane	556—700	—	650—750	—
Ethane	520—630	—	520—630	—
Propane	490—570	—	—	—
Ammonia	700—860	—	—	—

with the rates of flow of the gases, as well as with the size of the furnace tube, so that their ignition-temperatures are not so clearly defined as those of hydrogen, carbon monoxide, and the other gases.

Discussion.

The President asked whether the temperature of ignition would not be affected by varying the proportion of the gases; for example, if the rate of flow be so adjusted as to diminish the relative amount of oxygen, while keeping that of the hydrogen constant.

Professor Dixon replied that alteration of the proportion of the gases within wide limits had no effect on the ignition-temperature.

*58. "The alkaloids of Senecio latifolius."
By Henry Edgar Watt.

The author has made a chemical examination of *Senecio latifolius* (N.O. *Compositæ*), a poisonous plant which grows in South Africa, collected before flowering and also after flowering, and has isolated two new alkaloids of the formulæ $C_{18}H_{27}O_8N$ and $C_{18}H_{25}O_7N$ respectively, for which the names *senecifoline* and *senecifolidine* are proposed. The proportion of these substances present in the plant before flowering is equivalent to 1·20 per cent., whilst in the mature plant it only amounts to 0·49 per cent.

Senecifoline crystallises in colourless, rhombic plates, which melt at 194—195°, and has $[\alpha]_D$ +28°8′; it forms well-defined salts with nitric, hydrochloric, or hydriodic acids, and also an *aurichloride*. It can be decomposed by alkali into a hitherto undescribed dicarboxylic acid, $C_{10}H_{16}O_6$, which it is proposed to name *senecifolic acid*, and a new base, $C_8H_{11}O_2N$, for which the name *senecifolinine* is suggested.

Senecifolidine crystallises in colourless, rhombic plates, which melt at 212°, and has $[\alpha]_D$ −13°56′; it differs considerably from *senecifoline* in other physical respects, and forms salts corresponding with those mentioned above.

Discussion.

Dr. Watt stated, in reply to Dr. Bywaters, that Professor Cushny had kindly undertaken to work out the pharmacology of the alkaloids, and had already reported that one of them was poisonous to animals.

*59. "An interpretation of the Hantzsch-Werner hypothesis."
By Martin Onslow Forster and Frederick Percy Dunn.

From an investigation of the behaviour towards diazomethane displayed by some typical oximes, the authors were led to suggest

a possible explanation of the stereoisomerism occurring in this group of compounds.

Discussion.

Dr. Flürscheim suggested that Dr. Forster's interesting hypothesis might perhaps also apply to the diazo-compounds formulated by Hantzsch as *syn*- and *anti*-isomerides.

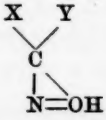
Dr. Morgan remarked that it would be of interest to know whether the supplementary valencies referred to by Dr. Forster were the ordinary valencies of oxygen and nitrogen indicated by the position of these elements in the periodic classification or the more elusive "Nebenvalenzen" postulated by Werner.

On the ordinary theory of valency, the isomeric diazo-derivatives fall into line with this conception of the structure of the *syn*- and *anti*-oximes, for the former series of isomerides contains the necessary grouping with an element of variable valency (shown in heavy type) contiguous to the double linking:

$$R\cdot N{:}\mathbf{N}\cdot OK$$
$$R\cdot N{:}\mathbf{N}\cdot SO_3K$$
$$R\cdot N{:}\mathbf{N}\cdot CN.$$

In the third case the required supplementary valencies could be obtained by a rearrangement of the cyanogen group.

Mr. Baly asked Dr. Forster whether he had considered the expression



as the extreme phase arising from his formula. This would make the oxygen atom quadrivalent, but there appears to be no objection to this, seeing that Dr. Forster's own formula postulated a valency on the part of the oxygen supplemental to the two normal valencies. Dr. Forster's formula, moreover, would seem to require a supplemental valency on the part of the carbon in addition to the normal four.

*60. **"The triazo-group. Part IX. Transformation of cinnamoylazoimide into cinnamenylcarbimide (cinnamenyl *iso*cyanate)." By Martin Onslow Forster.**

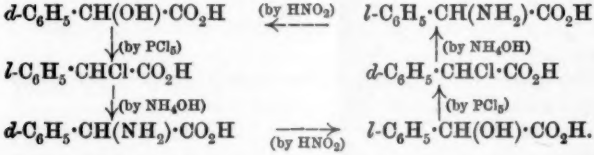
The production of cinnamenylcarbimide when cinnamoylazoimide loses nitrogen in absence of water leads to the conclusion that other

acyl azides owe their property of giving carbamates and carbamides with alcohols and amines respectively to intermediate formation of the respective carbimide.

***61. "Experiments on the Walden inversion. II. The interconversion of the optically active mandelic acids." By Alex. McKenzie and George William Clough.**

The preparation of *d*-phenylchloroacetic acid was described.

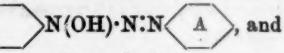
The following points have been investigated: action of water on *l*-phenylchloroacetic acid, action of water on salts of the optically active phenylchloroacetic acids, the displacement of chlorine in the active phenylchloroacetic acids by the amino-group, and the displacement of the amino-group in the active phenylaminoacetic acids by the hydroxyl group and by halogen groups. The interconversion of the active mandelic acids can be effected by a method different from that described previously, thus:



The striking feature in each one of these changes is the large amount of racemisation which always occurs.

62. "Diazohydroxylamino-compounds and the influence of substituting groups on the stability of their molecules." By Norman Leslie Gebhard and Herbert Bryan Thompson.

Arylhydroxylamines react with diazonium salts to form diazohydroxylamino-compounds or azohydroxyanilides, a class of substances which may be looked upon as hydroxyl derivatives of the diazoamino-compounds, in which the imino-hydrogen atom of the latter is replaced by a hydroxyl group. The tautomeric phenomena shown by unsymmetrical diazoamino-compounds is not observed with the diazohydroxylamino-compounds. A series of these substances, derived from *p*-tolylhydroxylamine and various diazonium compounds, has been prepared with the object of examining the general properties of these little-known substances, and comparing the various compounds prepared with one another, with the view of determining the effect of substituting groups of various types and in different positions in the molecule on

their general stability. The parent substance was benzenediazohydroxylamino-*p*-toluene,  , and a number of derivatives of this containing various substituting groups in the ring A have been prepared. The substituting groups used were methyl-, bromo-, nitro-, and carboxyethyl, whilst attempts were made to prepare the corresponding sulphonic acid and hydroxyl derivatives.

63. "Tetraketopiperazine. Part II." By Alfred Theophilus de Mouilpied and Alexander Rule.

The authors described the preparation and some of the reactions of tetraketopiperazine in a previous paper (*Trans.*, 1907, **91**, 176). Attempts have since been made to reduce the compound to a piperine derivative, but without success. Phosphorus pentachloride and phenylcarbimide are without action on the tetraketone.

The formation of coloured compounds during the preparation of the tetraketone had been noticed, and these are now found to be additive compounds of the sodium salt of tetraketopiperazine with sodium alcoholates.

They vary in colour from deep indigo-blue to bright purple, and are easily decomposed by water, but remain unchanged in dry ether.

64. "The miscibility of the pyridine bases with water and the influence of a critical-solution point on the shape of the melting-point curve." By Otto Flaschner.

The problem of the connexion between chemical constitution and mutual solubility of two liquids has been investigated in the case of the members of the pyridine and piperidine series combined with water. The width of the solubility ring for partly miscible liquids is taken as a comparable measure of the miscibility, whilst the miscibility of completely miscible pairs is defined by the width of that negative solubility ring which is obtained under a certain external influence, such as pressure or the solution of a third substance. The amount of this external action to be measured is that required to bring about under normal conditions the first appearance of two liquid phases. These considerations are illustrated by the miscibility of the three picolines and pipecolines with water.

The influence of the neighbourhood of a critical-solution point on the shape of the melting-point curve was discussed, and in the solutions of the zinc double salt of γ-picoline in the different aliphatic alcohols was found a convenient series of examples by means of which

the analogy between the shape of a melting-point curve and that of an isotherm of a vapour in the neighbourhood of the critical point can be demonstrated.

65. "The preparation of dichlorocarbamide." By Frederick Daniel Chattaway.

When dichlorocarbamide is prepared by passing chlorine through a cooled concentrated aqueous solution of carbimide, a yield of about 25 per cent. of the theoretical can with care be obtained. Unless, however, the process is very rapidly carried out, with efficient cooling, the quantity which separates falls much below this maximum. The loss is mainly due to hydrolysis of the dichlorocarbamide under the influence of the hydrogen chloride formed in the substitution. If this hydrogen chloride is removed immediately it is formed by combining it with some basic substance, hydrolysis is to a large extent prevented, and, if suitable quantities are used, over 75 per cent. of the amount of dichlorocarbamide theoretically obtainable from the carbamide used can be isolated in a pure dry state.

Details of the procedure recommended, in which the hydrogen chloride is removed by zinc oxide, were described.

66. "Thiotetrahydroquinazolines, methylenecarbamides, dicarbanilinomethylenediamines, and their homologues." By Alfred Senier and Frederick George Shepheard.

The interaction of arylthiocarbimides with arylmethylenediamines at temperatures from 150° to 200° results in the formation of cyclic compounds: cyclic carbamides and quinazolines. When the para-position in the aryl group of either the diamine or the thiocarbamide, or both of them, is occupied, thiotetrahydroquinazoline derivatives and a diarylthiocarbamide are formed. In all other instances, using thiocarbimides, and in all instances where the oxygen analogues, carbimides, are employed, the experiments being conducted at the temperatures mentioned, unstable cyclic methylenecarbamides or thiocarbamides are probably formed, and at the same time a diarylcarbamide or thiocarbamide. That these unstable cyclic carbamides are actually formed, although they were identified only by the products of their hydrolysis, is rendered extremely probable by the fact that in two instances, employing a different reaction, namely, the substitution of methyleneaniline for a methylenediamine, the authors succeeded in isolating them and proving their instability.

At the ordinary temperature, the course of the reactions is in

agreement with previous experiments; carbanilino- or thiocarbanilino-methylenediamines or their homologues are always formed (Senier and Goodwin, *Trans.*, 1901, **79**, 254; 1902, **81**, 283).

67. "**The distillation of butter fat, cocoanut oil, and their fatty acids.**" By **Kenneth Somerville Caldwell** and **William Holdsworth Hurtley**.

The authors are of opinion that fats and fatty acids have no boiling points in the vacuum of the cathode light, but that for any particular substance a temperature can be selected at which evaporation occurs at a speed convenient for fractional distillation.

Butter fat, cocoanut oil, and their fatty acids were distilled in the vacuum of the cathode light. The lowest fraction obtained from butter fat distilled with the bath temperature at 250—270° and inner thermometer at 187—210°. Tributyrin distils rapidly with the bath temperature at 127° and inner thermometer at 107°. For this and other reasons, it is concluded that butter does not contain tributyrin. The iodine numbers yielded by the various fractions seem to indicate that there is little or no triolein in butter fat. Lauric acid forms at least 60 per cent. of the fatty acids in cocoanut oil, whilst it could not be detected in butter; this method of distillation enabled the authors to detect with ease the presence of 10 per cent. of cocoanut oil in butter. The presence of palmitic acid in cocoanut oil has been questioned by Ulzer (*Chem. Revue*, 1899, 203), but the authors isolated several grams of this acid from cocoanut oil.

68. "**Note on the detection of white or ordinary phosphorus in the igniting composition of lucifer matches.**" By **Thomas Edward Thorpe**.

As the White Phosphorus Matches Prohibition Act, 1908, will throw upon Officers of Customs and the Inspectors under the Factory and Workshop Act, 1901, the duty of sampling importations of matches and of materials in use in match factories, the author has examined the methods by which the presence of ordinary phosphorus in the igniting composition of lucifer matches containing phosphorus sesquisulphide may be established, and he finds that the most direct and most certain test is to isolate the phosphorus as such, which is conveniently effected by gently heating the composition in a vacuum, when the phosphorus sublimes and may be readily recognised by its physical characteristics.

69. "Intramolecular rearrangement of the diphenylamine sulphoxides." (Preliminary note.) By Edward de Barry Barnett and Samuel Smiles.

When the yellow tetranitro-, 3 : 9-dinitro-, and *iso*dinitro-diphenylamine sulphoxides are treated with suitable reagents—for example, an alcoholic solution of hydrogen chloride—brick-red or chocolate-coloured, crystalline substances are formed. According to the conditions of the reactions, the dark-coloured compounds so obtained are either isomeric with the sulphoxides or differ from them by the content of a molecule of water. The evidence hitherto collected shows that these substances, although they are not of pronounced basic character, contain the ortho-quinonoid sulphonium structure, and this view is confirmed by the fact that the unsubstituted diphenylamine sulphoxide is readily converted by aqueous acids into salts of phenazothionium. The depression of the basic properties in the nitro-derivatives is explained by the influence exerted on the quadrivalent sulphur by the acidic substituents.

70. "A crystalline bleaching powder."
By Kennedy Joseph Previté Orton and William Jacob Jones.

A basic hydrated compound of calcium chloride and calcium hypochlorite, which separates on cooling moderately concentrated (about 2*N*) solutions of bleaching powder, was described. This substance has been obtained in large, prismatic crystals, the properties of which closely resemble those of bleaching powder. On the other hand, from very highly concentrated solutions of bleaching powder (about 4*N*), a hydrated calcium hypochlorite separates at low temperatures.

71. "The action of carbon dioxide on nitrites."
By Ernest Robert Marle.

The contradiction in the results obtained by Marie and Marquis (*Compt. rend.*, 1904, **138**, 367) and Meunier (*Compt. rend.*, 1903, **137**, 1264; compare also Papasogli, *Gazzetta*, 1881, **11**, 277; Moody, *Proc.*, 1903, **19**, 240) in investigating the action of carbon dioxide on nitrites seems to be partly due to the unsuitability of potassium iodide and starch as a test for traces of nitrites unless special precautions be taken.

Warington (*Chem. News*, 1885, **51**, 39) finds that one of the most delicate tests for nitrous acid is the coloration produced with α-naphthylamine (Griess).

Carbon dioxide, prepared from marble and hydrochloric acid, was washed by passing through water in two Drechsel bottles, and was then passed through 10 per cent. aqueous potassium nitrite in a Cloez washing bottle, the construction of which is such that it is unlikely that liquid will be mechanically carried over by the stream of gas. It was then passed into water or potassium carbonate for periods varying from one to six hours.

In every case the coloration with potassium iodide and starch seemed slightly greater than that produced by the reagents alone. With α-naphthylamine, a faint pink coloration resulted after a few minutes.

To guard against the possibility of mistaking nitrite, mechanically carried over, for nitrous acid, a dry Arnold absorption apparatus was inserted between the Cloez bottle and the final flask. A slight mist appeared on the inside of the absorption bulbs, which, when washed out with water, proved faintly acid to litmus, and with α-naphthylamine gave a full red colour, appearing in about three minutes. The water in the final flask was neutral (after boiling), and gave with α-naphthylamine a faint coloration, appearing in about fifteen minutes.

From the data in Warington's paper, the quantity of nitrogen (as nitrous acid) removed by one litre of carbon dioxide is probably less than one two-hundredth of a milligram. The reduction of very dilute potassium permanganate by the solution in the final flask leads to a similar figure.

72. "Estimation of primary, secondary, and tertiary amines. Part I." By John Joseph Sudborough and Harold Hibbert.

The method outlined by the authors some years ago (*Proc.*, 1904, **20**, 165) for the estimation of primary, secondary, and tertiary amines has been found capable of general application. Phenetole may be substituted for amyl ether as solvent. The procedure was identical with that followed by the authors in the estimation of hydroxyl groups in carbon compounds (*Trans.*, 1904, **85**, 933).

Quantitative results have been obtained with the following substances: phenyl-α-naphthylamine, phenyl-β-naphthylamine, ββ-dinaphthylamine, diphenylamine, ethylaniline, methylaniline, β-naphthylamine, *p*-toluidine, *p*-chloroaniline, dimethylaniline, diethylaniline, and tetramethyl-*p*-diaminodiphenylmethane.

73. "The condensation of ketones and aldehydes with the sodium derivative of ethyl cyanoacetate." By Walter Norman Haworth.

The author discussed the nature of the condensation of ethyl cyanoacetate with certain representative aldehydes and ketones.

74. "Experiments on the constitution of the aloins. Part I." (Preliminary note.) By Robert Robinson and John Lionel Simonsen.

In view of the recent publication of a memoir by Oesterle and Tisza (*Schweiz. Wochschr. Chem. Pharm.*, 1908, **46**, 701) on the subject of rhein, the authors communicated some of the results obtained during the last two years in connexion with an investigation of the constitution of the various aloins, and undertaken with the permission and assistance of Dr. Jowett.

The oxidation of the acetyl derivative of barbaloin with chromic acid leads to the formation of *diacetylrhein*, $C_{14}H_5O_2(OAc)_2 \cdot CO_2H$ (m. p. 245°), and other substances. The investigation and analysis of rhein and its derivatives have conclusively shown that this substance has the composition $C_{15}H_8O_6$, and is a *dihydroxyanthraquinonecarboxylic acid.*

This view is based on the following facts: (1) The substance has all the properties of an acid, and is soluble in the alkaline carbonates and even in sodium acetate. It yields a *methyl* ester, $C_{14}H_5O_2(OH)_2 \cdot CO_2Me$ (m. p. 174°), and *ethyl* ester, $C_{14}H_5O_2(OH)_2 \cdot CO_2Et$ (m. p. 159°), insoluble in cold sodium carbonate.

(2) Rhein yields a diacetate, and prolonged treatment with acetylating agents failed to introduce any further acetyl groups.

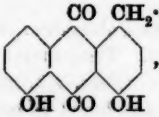
(3) Methylation of rhein with methyl sulphate and potassium hydroxide yields *dimethylrhein*, $C_{14}H_5O_2(OMe)_2 \cdot CO_2H$ (m. p. 281—282°), which is also a strong acid, readily soluble in sodium carbonate or sodium acetate, and incapable of acetylation or benzoylation. It would appear that the methylrhein (m. p. 288°) which Oesterle and Tisza (*loc. cit.*) describe is identical with this substance, and their observation that it is insoluble in potassium hydroxide may possibly be due to the fact that its potassium salt is very sparingly soluble in potassium hydroxide.

Dimethylrhein yields an *ethyl* ester, $C_{14}H_5O_2(OMe)_2 \cdot CO_2Et$ (m. p. 185—187°).

When treated with thionyl chloride, dimethylrhein yields the corresponding *chloride*, $C_{14}H_5O_2(OMe)_2 \cdot COCl$ (m. p. 190°), which on treatment with concentrated ammonia yields *dimethylrheinamide*, $C_{14}H_5O_2(OMe)_2 \cdot CO \cdot NH_2$ (m. p. 286°).

Now since aloe-emodin is a trihydroxymethylanthraquinone and yields rhein on oxidation, it follows that one of the hydroxyl groups is situated in the methyl group, and the authors are therefore of the opinion that aloe-emodin is a *dihydroxyanthraquinolcarbinol*.

The data at present available are not sufficient to prove conclusively the position of the several groups in rhein and aloe-emodin, but there is much reason to believe that rhein is *chrysazincarboxylic acid*, and that the carbonyl group occupies an α-position. The important facts on which these views are based are that barbaloin gives tetranitrochrysazin on treatment with nitric acid, and that aloe-emodin gives α-methylanthracene on distillation with zinc dust. If chrysazin is 1 : 8-dihydroxyanthraquinone, then aloe-emodin would have the constitution :



and rhein would be the corresponding acid.

The authors consider that aloetic acid, which results from the oxidation and nitration of aloin, is not tetranitroanthraquinone, but dinitrosodinitrochrysazin, and that aloechrysin, produced by the oxidation of aloin with chromic acid, is the aldehyde intermediate between the primary alcohol aloe-emodin and the carboxylic acid rhein.

75. "The constituents of Canadian hemp. Part II. Cynotoxin." (Preliminary note.) By Horace Finnemore.

The aqueous solution of the alcoholic extract of the root of commercial *Apocynum cannabinum* (*Trans.*, 1908, **92**, 1514) yields on extraction with chloroform, after removing the apocynin with ether (*loc. cit.*), a relatively small quantity of an intensely active substance, which produces symptoms identical with those caused by the drug itself.

Cynotoxin, $C_{20}H_{28}O_6$, is a well-defined, colourless substance, which crystallises in small, apparently rhombic pyramids, and melts and decomposes at about 165°. It is sparingly soluble in water and the usual organic solvents, and extremely bitter in taste. Pharmacological investigation by Mr. P. P. Laidlaw, M.B., has shown that it is an extremely potent drug of the digitalis class and that the pharmacological properties of apocynin (acetovanillone, *loc. cit.*) are negligible. The chemical and pharmacological properties of cynotoxin are still under investigation; it is already evident, however, that it is a dilactone, either of Kiliani's digitic acid, $C_{20}H_{32}O_8$ (*Ber.*, 1891, **24**, 339), or of a closely related isomeride.

ADDITIONS TO THE LIBRARY.

I.—*Donations.*

Guttmann, *Oscar.* The manufacture of explosives. Twenty years' progress. Four Cantor Lectures delivered at the Royal Society of Arts in November and December, 1908. pp. viii + 84. ill. London 1909. (*Recd.* 20/2/09.) From the Author.

Martindale, *W. Harrison,* and **Westcott,** *W. Wynn.* The extra pharmacopœia. 13th edition. pp. xl + 1164. London 1908. (*Recd.* 18/2/09.) From Dr. W. H. Martindale.

Owen, *F. A.* The dyeing and cleaning of textile fabrics. Based partly on notes of *H. C.* **Standage.** pp. vi + 253. New York 1909. (*Recd.* 29/2/09.)

From the Publishers: Messrs. John Wiley & Sons.

Schryver, *Samuel Barnett.* The general characters of the proteins. pp. x + 86. London 1909. (*Recd.* 4/3/09.)

From the Publishers: Messrs. Longmans, Green & Co.

Tschelinzeff, *W.* Individuelle magnesiumorganische Verbindungen, und ihre Umwandlungen in Oxonium- und Ammonium-Komplexe. pp. iv + 271. Moscow 1908. [In Russian.] (*Recd.* 18/2/09.)

From Dr. A. McKenzie.

II.—*By Purchase.*

Bruni, *Giuseppe.* Feste Lösungen und Isomorphismus. pp. vi + 130. Leipzig 1908. (*Recd.* 3/3/09.)

Ditmar, *Rudolf.* Die Analyse des Kautschuks, der Guttapercha, Balata und ihrer Zusätze, mit einschluss der Chemie der genannten Stoffe. pp. viii + 288. ill. Wien 1909. (*Recd.* 17/2/09.)

Friend, *J. Newton.* The theory of valency. pp. xiv + 180. London 1909. (*Recd.* 27/1/09.)

Hall, *Alfred Daniel.* The soil. 2nd edition. pp. xv + 311. ill. London 1908. (*Recd.* 20/1/09.)

Haller, *Albin.* Les récents progrès de la chimie. (Troisième série.) Conférences faites au Laboratoire de Chimie organique de la Sorbonne, sous la direction de A. Haller. pp. 261. Paris 1908. (*Recd.* 5/2/09.)

Hubert, *Paul.* Plantes à parfums. pp. xii + 610. ill. Paris 1909. (*Recd.* 17/2/09.)

Jörgensen, *S. M.* Die Entdeckung des Sauerstoffes. Aus dem Dänischen von *Vilhelm* **Ortwed** und *Max* **Speter.** (Sammlung, Vol. XIV.) Stuttgart 1909.

Schenck, *Rudolf.* Physikalische Chemie der Metalle. Sechs Vorträge über die wissenschaftlichen Grundlagen der Metallurgie. pp. vi + 193. ill. Halle a. S. 1909. (*Recd.* 17/2/09).

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Metropole, at 6.30 for 7 o'clock, on Thursday, March 25th, 1909 (the day fixed for the Annual General Meeting).

The price of the tickets will be One Guinea each, including wine.

All applications for tickets must be received not later than Thursday, March 18th next.

Tickets will be forwarded to Fellows on receipt of a remittance for the number required, made payable to "Mr. S. E. Carr" and addressed to the Assistant Secretary, Chemical Society, Burlington House, W.

At the Annual General Meeting to be held on Thursday, March 25th, at 4 p.m., the PRESIDENT will deliver an address entitled: "Elements and Electrons."

At the next Ordinary Meeting, on **Thursday**, March 18th, 1909, at 8.30 p.m., the following papers will be communicated:

"Iodine dioxide." By M. M. P. Muir.

"The constituents of the rhizome of *apocynum androraemifolium*." By C. W. Moore.

"The action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part IV. Derivatives of dihydroxyphenylacetic, -glycollic, and -glyoxylic acids." By G. Barger and A. J. Ewins.

"Studies in the azine series. Part I. The constitution of safranine." By J. T. Hewitt, S. H. Newman, and T. F. Winmill.

"The condensation of amides with esters of acetylenic acids." By S. Ruhemann.

"A polarimetric method of identifying chitin." By J. C. Irvine.

"Studies in asymmetric synthesis. Part VII. The influence of the *d*-amyl group." By A. McKenzie and H. A. Müller.

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Issued 26/3/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 354.

Thursday, March 18th, 1909, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. F. P. Dunn, J. T. Furnell, J. H. Jeffery, P. May, A. B. Robertson, and W. O. Wootton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Albert Riley Blackburn, B.Sc., Marshville, Derby Road, Widnes, Lancs.
Walter Campbell, Albert House, Westcliff-on-Sea.
Daniel Little Couch, 9, Charlmont Road, Tooting, S.W.
Edward Gordon Couzens, B.Sc., 47, Allfarthing Lane, Wandsworth.
Francis Clifford Dyche-Teague, B.Sc., 8, Mount Road, Hendon, N.W.
Charles James Grist, Apsley House, Banstead, Surrey.
Leonard Angelo Levy, B.A., B.Sc., 60, Priory Road, West Hampstead, N.W.
Robert Müller, Royal College of Science, South Kensington, S.W.
Frederick Leigh Okell, c/o Straits Trading Co., Singapore.
John Webster, 44, Holmewood Gardens, Brixton Hill, S.W.

A Certificate has been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of Mr.:

Henry Ernest John Bletcher, Winnipeg, Manitoba.

The PRESIDENT announced that those Fellows desirous of supporting the International Memorial to the late Marcelin Berthelot should forward their subscriptions to M. H. Bocquillon-Limousin, 2^bis Rue Blanche, Paris.

Of the following papers, those marked * were read:

*76. "Liquid and solid radium emanation."
By Robert Whytlaw Gray and Sir William Ramsay, K.C.B.

In the course of some recent work on radium emanation, the authors have prepared this gas in a state of fair purity, and it appeared worth while trying to liquefy it by pressure. It was therefore introduced into a very fine-bore capillary tube of 0·08 mm. diameter, fitted in a compression apparatus of the kind used by Ramsay and Young, and compressed to a smaller volume. When sufficiently small, there was seen at the conical point of the tube a minute column of liquid, easily visible under low microscopic power. By altering the volume, more or less liquid could be condensed. In short, by transmitted light all the usual phenomena of condensing and evaporating a liquid were observed. The liquid is colourless, and indistinguishable from water, or from, say, liquefied argon or xenon. If, however, the illumination from behind be extinguished, and the tube be viewed by its own illumination, even in broad daylight, the liquid is visible as a greenish or bluish-green phosphorescent layer, not very luminous, but more luminous than the gaseous layer. Its vapour pressures were measured at −10° (boiling point of sulphur dioxide), 0° (melting point of ice), 12·8° and 16·2° (atmospheric temperatures), and 47° (boiling point of carbon disulphide). But the gas was not quite pure; pressure rose during condensation. Allowing approximately for this, Ramsay and Young's rule was made use of to calculate the vapour-pressure curve. The pressures and temperatures are as follows:

P.	*T.*	*P.*	*T.*
100 mm.	−74·5°	1000 mm.	−43·1°
200 ,,	−66·1	2000 ,,	−31·0
500 ,,	−53·6	5000 ,,	−12·8
760 ,,	−48·5	10,000 ,,	+1·5

These vapour pressures must be taken as only approximate. The density of the liquid could be estimated, too, with rough approximation, as about 7, assuming that of the gaseous emanation to be 100 times that of gaseous hydrogen; it is considerably higher than that of xenon, namely, 3·52.

This liquid, as remarked, is only feebly phosphorescent. But if cooled by touching the tube with cotton-wool moistened with liquid

air, it turns brilliant; the colour changes to a bright steel-blue, and it blazes with light. Continued application of liquid air changes the colour, first to white, then to yellow, and finally to orange. Through the microscope it looks like a brilliant little arc light. On removing the liquid air, the reverse change occurs; the orange light becomes yellow, then white, and then blue; and there seems to be some sort of disturbance in the tube, as if crystals of a solid were disintegrating; then appears the faintly phosphorescing liquid, and if the volume be large enough, the still more faintly phosphorescing gas. Transmitted light shows merely a colourless liquid, as before. These changes can be reproduced again and again; they were exhibited to several persons in the laboratory. There is no doubt that the substance which is brilliantly luminous is a solid.

In *Nature* (1909, **79**, 457), Professor Rutherford describes experiments in which he obtained such "a brilliant point of phosphorescent light"; and he measured the temperature at which the "initial condensation of the emanation" occurred at atmospheric pressure; he found it to be $-65°$. In the light of the above experiments, it is difficult to say what he was observing; probably, the solidifying point of the emanation, although he speaks of having seen "small drops of liquid emanation on the walls of the capillary."

***77. "Optically active substances which contain no asymmetric atom." (Preliminary note.) By William Henry Perkin, William Jackson Pope, and Otto Wallach.**

The possible existence of optically active substances which contain no asymmetric atom in the molecule was foreseen many years ago by van't Hoff, but the attempts hitherto made to obtain such compounds have been unsuccessful. All the constitutional formulæ at present assigned to substances which exhibit optical activity in the liquid state indicate the presence of one or more asymmetric atoms in the molecule.

Some time ago Perkin and Pope (Trans., 1908, **93**, 1082) synthesised 1-methyl*cyclo*hexylidene-4-acetic acid,

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix}H\\CO_2H\end{matrix}\text{,}$$

and pointed out that, on the basis of the tetrahedral environment of the carbon atom in methane, this substance possesses an enantiomorphous molecular configuration, and should hence exist in optically active forms. The constitutional formula, however, comprises no atom which can be described as asymmetric, no matter which definition of an asymmetric atom be adopted. The authors have now succeeded in

separating from the synthetic and optically inactive acid a pure optically active modification of 1-methyl*cyclo*hexylidene-4-acetic acid by the method described below.

To a hot aqueous solution of two molecular proportions of externally compensated sodium 1-methyl*cyclo*hexylidene-4-acetate is added a hot aqueous solution of very slightly less than one molecular proportion of brucine hydrochloride; during admixture alcohol is added in just sufficient quantity to prevent the solution becoming turbid owing to separation of an oily salt. On cooling and scratching with a glass rod, rather less than one-half of the acid separates as crystalline *brucine* lævo-1-*methyl*cyclo*hexylidene*-4-*acetate*,

$$C_{23}H_{26}O_4N_2,C_9H_{14}O_3,2H_2O,$$

whilst most of the dextro-component of the acid remains in solution as sodium salt. After crystallisation from dilute alcohol to remove adherent mother liquor, the pure salt is obtained in colourless needles melting at 97°; it shows the specific rotatory power $[\alpha]_D$ −58·1° in a 0·8 per cent. alcoholic solution.

lævo-1-*Methyl*cyclo*hexylidene*-4-*acetic acid* is obtained from the brucine salt by addition of hydrochloric acid to its hot aqueous solution; after crystallisation from light petroleum the optically active acid melts at 52·5°, and shows the specific rotatory power $[\alpha]_D$ −81° in alcoholic solution. On treatment with fuming hydrobromic acid it yields the potentially inactive 4-bromo-1-methyl*cyclo*hexyl-4-acetic acid,

$$\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!CBr\cdot CH_2\cdot CO_2H,$$

which melts at 78°.

Discussion.

Dr. Tutton asked whether Prof. Pope had been able to measure the crystals, and if so, whether he had found them to belong, as usual in cases of optical activity, to one of the eleven enantiomorphous classes which exhibit lower symmetry than the maximum symmetry of their system.

Dr. McKenzie referred to the work of Marckwald and Meth in this connexion. Reference was also made to the fact that the configurations assigned to the active inosites represent these compounds as not possessing an asymmetric atom.

Replying to Dr. Tutton, Prof. Pope stated that attempts were being made to examine derivatives of the active acid goniometrically in order to ascertain whether Pasteur's law holds in connection with the crystalline form of substances which owe their optical activity

to the new kind of asymmetry now discovered. In reply to Prof. Armstrong, it was observed that although the molecule contains no asymmetric atom, an asymmetric system forms part of the molecular configuration, and that the optical activity arises from the enantiomorphism thus introduced. In connexion with Dr. McKenzie's remarks, Prof. Pope observed that no doubt can now exist that the acid described by Marckwald as 1-methyl*cyclo*hexylidene-4-acetic acid is really 1-methyl*cyclo*hexene-4-acetic acid, the molecule of which contains an asymmetric carbon atom. The configuration assigned to inosite certainly contained asymmetric carbon atoms.

***78. "The constituents of the rhizome of Apocynum androsæmifolium." By Charles Watson Moore.**

The material employed in this investigation was the rhizome of *Apocynum androsaemifolium*, Linné. An alcoholic extract of the rhizome, when distilled in a current of steam, yielded small amounts of an essential oil and acetovanillone. The non-volatile constituents of the rhizome, as obtained after treating the alcoholic extract with steam, consisted of a brown resin (A) insoluble in either hot or cold water; a brown resin (B) soluble in the hot aqueous liquid, but which was slowly deposited on standing; and material which remained dissolved in the cold aqueous liquid. The brown resin (A) yielded small quantities of ipuranol, $C_{28}H_{33}O_2(OH)_2$ (m. p. 285—290°), and acetovanillone; palmitic, stearic, oleic, and linolic acids, and a large quantity of unsaponifiable material. From the latter, two new alcohols, *androsterol*, $C_{30}H_{49}\cdot OH$ (m. p. 208—210°), and *homoandrosterol*, $C_{27}H_{43}\cdot OH$ (m. p. 192°), were obtained, whilst the presence of a third alcohol was proved by the isolation of its *bromoacetyl* derivative (m. p. 265—268°). Androsterol yields an *acetyl* derivative (m. p. 212—214°) and a *monobromoacetyl* derivative (m. p. 228—230°). *Acetylhomoandrosterol* melts at 236°. The brown resin (B) yielded a further small quantity of acetovanillone. The portion of the alcoholic extract of the rhizome which was soluble in cold water, and from which the above-described resins had been removed, contained large amounts of sugar and tannin. It yielded a quantity of acetovanillone (m. p. 115), which was also present in the form of its glucoside, *androsin*, $CH_3\cdot CO\cdot C_6H_3(O\cdot CH_2)\cdot O\cdot C_6H_{11}O_5,2H_2O$ (m. p. 218—220°), and a new substance, *apocynamarin*, $C_{28}H_{36}O_6,2H_2O$ (m. p. 170—175°), which possesses an intensely bitter taste, is highly toxic, and represents the chief active constituent of the rhizome.

***79. "The action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part IV. Derivatives of dihydroxyphenyl-acetic, -glycollic, and -glyoxylic acids." By George Barger and Arthur James Ewins.**

Starting from ethyl 3 : 4-methylenedioxymandelate, which is more readily obtained from piperonalcyanohydrin than the corresponding acid (previously obtained by Lorenz, *Ber.*, 1881, **14**, 793), the authors have prepared a number of methylene ethers and cyclic carbonates related to 3 : 4-dihydroxymandelic acid, $C_6H_3(OH)_2 \cdot CH(OH) \cdot CO_2H$, and to 3 : 4-dihydroxyphenylglyoxylic acid, $C_6H_3(OH)_2 \cdot CO \cdot CO_2H$, and also these acids themselves.

3 : 4-Dihydroxymandelic acid and its derivatives are very soluble in water, quite unlike epinephrine (adrenaline), which also contains the complex $C_6H_3(OH)_2 \cdot CH(OH) \cdot$. Dihydroxymandelic acid is much less stable than the corresponding keto-acid.

***80. "Studies in the azine series. Part I. The constitution of safranine." By John Theodore Hewitt, Sidney Herbert Newman, and Thomas Field Winmill.**

Phenosafranine has the composition of a salt (chloride) of phenylphenazonium. According to Bernthsen the two amino-groups are symmetrically situated, whilst Witt supposed that one was in the phenyl group, only one being attached to the phenazine nucleus. The question was apparently decided in favour of Bernthsen's formula by Körner and Schraube, who obtained identical dialkylsafranines by the oxidation of (*a*) one molecule of *as*-dialkyl-*p*-phenylenediamine with two molecules of aniline, and (*b*) one molecule each of *p*-phenylenediamine, aniline, and its dialkyl derivative.

More recently P. Barbier and P. Sisley (*Ann. Chim. Phys.*, 1908, [viii], **13**, 96) have stated that phenosafranine, as prepared by oxidising *p*-phenylenediamine with aniline, consists essentially of the asymmetric compound mixed with small amounts of an isomeride having the structure given by Bernthsen.

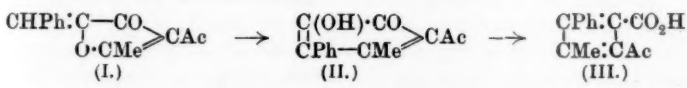
The present authors find that the hydroxyaposafranone obtained from safranine is identical with that prepared by Jaubert's method from nitrosophenol and *m*-hydroxydiphenylamine (*Ber.*, 1895, **28**, 273), since the acetyl derivatives prepared from both specimens melt at 271° (uncorr.) whether alone or mixed (Fischer and Hepp give 265—268°: *Ber.*, 1897, **30**, 401).

The synthesis of an asymmetric phenosafranine by oxidation of aniline with 2 : 4′-diaminodiphenylamine described by Barbier and Sisley (*loc. cit.*, p. 102) could not be realised, any safranine obtained by them probably owing its origin to admixed 4 : 4′-diaminodiphenylamine, since potassium dichromate converts 2 : 4′-diaminodiphenylamine into aminophenazine whether aniline be present or not.

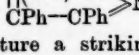
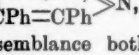
The experiments recorded are only compatible with the symmetrical (Bernthsen's) formula for phenosafranine.

***81. "The condensation of amides with esters of acetylenic acids." By Siegfried Ruhemann.**

Ruhemann and Merriman (Trans., 1905, **87**, 1383) have shown that acetylacetone condenses with phenylpropiolyl chloride to a yellow furfuran derivative (I); this readily changes into its red isomeride (II), which, with bases, forms blue salts, and with hot sodium carbonate yields a colourless acid (III) isomeric with (I) and (II). These changes were represented thus:



(I.) (II.) (III.)

The correctness of these formulæ follows from the fact that ethyl phenylpropiolate condenses with sodiobenzamide to a coloured compound, $C_{16}H_{11}O_2N$ (dark red needles, m. p. 184°), which, with alkalis, forms blue salts; the substance which is to be regarded as *diphenyldiketopyrroline*,  or  , shows in its properties and structure a striking resemblance both to the compound (II) and the similarly constituted substances (see Ruhemann and Merriman, *loc. cit.*) and to isatin. On boiling with potassium hydroxide, it decomposes quantitatively into ammonia, oxalic acid, and deoxybenzoin.

Discussion.

Dr. Hewitt fully agreed with Dr. Ruhemann that in the compounds he described the sodium probably attached itself to an oxygen atom. He ventured to suggest this might be equally well expressed by a rearrangement of the conjugate double linkings as by the formation of a bridged ring.

***82. "Studies in asymmetric synthesis. Part VII. The influence of the *d*-amyl group." By Alex. McKenzie and Hermann August Müller.**

The action of magnesium organic compounds on *d*-amyl pyruvate and *d*-amyl benzoylformate respectively has been examined. The asymmetric synthesis of *d*-lactic acid by the reduction of *d*-amyl pyruvate was described.

It appears that the more optically active is the directing asymmetric agent the more pronounced is the asymmetric synthesis.

Attempts to substitute gallic acid for 3-nitrophthalic acid in order to effect the separation of *d*-amyl alcohol from fusel oil were not successful.

***83. "Contributions to the chemistry of cholesterol and coprosterol." By Charles Dorée.**

The author has investigated the action of ozone on the following cholesterol derivatives: cholestenone, the acid $C_{27}H_{44}O_4$, β-cholestanol, coprosterol, ψ-coprosterol, and the ketones corresponding with these and α-cholestanol. All of these with the exception of α-cholestanol, which is indifferent, react with ozone, and the determination of the ozone numbers of these compounds confirms generally the view of Molinari (*Ber.*, 1908, **41**, 2782) that a second double linking is present in the cholesterol molecule. For this there is no other chemical evidence, and the addition of the second molecule of ozone has now been shown to take place with considerable difficulty, so that this may not be a case of simple addition, but of a development of some grouping in the molecule under the influence of ozone with subsequent addition.

Reasons were given for ascribing to the compound previously obtained by the action of phenylhydrazine on coprostanone (*Trans.*, 1908, **93**, 1627) a constitution of the carbazole type. A crystalline *nitrosite* was prepared and analysed.

84. "Iodine dioxide." By Matthew Moncrieff Pattison Muir.

Reference was made to the work of Millon, in 1844, and of Kämmerer, in 1861, on an oxide of iodine said to be composed of iodine and oxygen united in the ratio of I : 2O, none of which work satisfactorily proved the existence of the compound.

The compound IO_2, or I_2O_4, has been prepared by the dehydration and partial deoxidation of iodic acid by heating that acid with

concentrated sulphuric acid. Two methods of analysing iodine dioxide were described. It was shown that the interactions of this oxide and oxalic acid, in the presence of sulphuric acid, at 100°, and with boiling water, are severally represented by the equations:

$$(1)\ I_2O_4 + 4C_2H_2O_4 = I_2 + 4H_2O + 8CO_2$$

and $$(2)\ 5I_2O_4 + 4H_2O = 8HIO_3 + I_2.$$

Iodine dioxide is a pale yellow, crystalline solid of specific gravity 4·2; it is decomposed at about 130° into iodine and oxygen. The molecular weight of the compound has not been determined. The reactions of the oxide with acids and with various reagents were described; in most of these interactions, iodine pentoxide and iodine are produced. Iodine dioxide is slightly soluble in cold concentrated sulphuric acid; 100 c.c. of the acid dissolve 1·54 grams of the oxide at 15° to 20°. Inasmuch as iodine dioxide forms a compound with sulphur trioxide having the composition $I_2O_4,3SO_3$, the oxide has slightly basic properties. This compound is not decomposed by heating to 100°, but begins to give off iodine, oxygen, and sulphur trioxide at about 120°.

Incidentally, it was shown that iodic anhydride and sulphur trioxide combine, when heated together at 100°, to form a compound which has the composition $I_2O_5,2SO_3$.

The slightly basic characters of the two oxides of iodine emphasise the connexions between iodine and manganese.

85. "A polarimetric method of identifying chitin."
By James Colquhoun Irvine.

A solution of chitin in concentrated hydrochloric acid is slowly transformed into glucosamine hydrochloride at the ordinary temperature. The change is greatly accelerated by keeping the solution at 45°, being then complete in eight to ten hours. Under these conditions, the hydrolysis is quantitative, no humic compounds or other colouring matters are produced, and thus the reaction may be followed polarimetrically. As chitin is lævorotatory, the conversion into glucosamine hydrochloride is accompanied by a characteristic "inversion," the average result (calculated on the initial concentration) being:

$$[\alpha]_D^{20}\ -14{\cdot}1^\circ \longrightarrow [\alpha]_D^{20}\ +56{\cdot}0^\circ.$$

The results obtained showed great uniformity, and thus the method can be applied as a test for chitin, which is capable of positively identifying 0·1 gram of the substance.

The constancy of rotatory power observed with specimens of chitin

prepared from widely different sources affords strong evidence that the substance is a definite compound of uniform composition and structure. As "spongin" and "keratin" did not show any optical inversion during hydrolysis, it seems doubtful if these substances are in any way related to chitin. The different formulæ suggested for the latter compound have been examined in their relationship to the polarimetric results, the best agreement being given by the expression $(C_{30}H_{50}O_{19}N_4)_m$ in which aminoglucose and acetylaminoglucose residues are present in the proportion of one to three.

86. "The conversion of *d*-α-methyl*iso*serine into *d*-α-methylglyceric acid." By Francis William Kay.

In the course of investigating the action of nitrosyl bromide on the β-amino-acids, it was found that α-methyl*iso*serine (β-amino-α-hydroxy-*iso*butyric acid) was converted into β-bromo-α-methyl-lactic acid (β-bromo-α-hydroxy*iso*butyric acid), which melts at 102—103° (uncorr.), and has already been described by Melikoff (*Annalen*, 1886, **234**, 213):

$$NH_2\cdot CH_2\cdot CMe(OH)\cdot CO_2H \xrightarrow{NOBr} CH_2Br\cdot CMe(OH)\cdot CO_2H.$$

d-α-Methyl*iso*serine by a similar treatment yields d-*β-bromo-α-methyl-lactic acid*, which crystallises from benzene in needles, m. p. 114° (uncorr.), and has $[\alpha]_D^{20} + 7{\cdot}40°$ in approximately 10 per cent. aqueous solution.

The action of the theoretical amount of alcoholic potassium hydroxide (2 mols.) converts the above bromo-acid into *potassium* d-α-*methylglycidate*,

$$CH_2Br\cdot CMe(OH)\cdot CO_2H \longrightarrow O\begin{array}{l}<CH_2\\ \ \ CMe\cdot CO_2K\end{array}.$$

This salt crystallises in silvery leaflets, and has $[\alpha]_D^{20} - 17{\cdot}57°$.

When potassium *d*-α-methylglycidate is heated with water to 100°, it undergoes hydroxylation and is transformed into *potassium* d-α-*methylglycerate*:

$$O\begin{array}{l}<CH_2\\ \ \ CMe\cdot CO_2K\end{array} \longrightarrow OH\cdot CH_2\cdot CMe(OH)\cdot CO_2K$$

The aqueous solution of this salt has a specific rotation of $-4{\cdot}00°$.

87. "The action of steam on iron." (Preliminary note.) By John Albert Newton Friend.

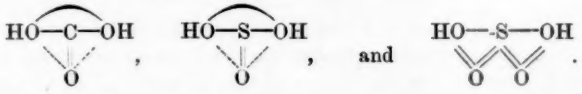
The author has studied the action of steam on iron at temperatures ranging from 100° to a red heat. It is found that pure, carbon

dioxide-free steam has no action on pure iron until those temperatures are reached at which the steam begins to dissociate, when a black oxide (presumably Fe_3O_4) is produced.

The conclusion is drawn that the usual statement that steam is decomposed by red-hot iron is not true. The reaction really takes place in two stages, involving (i) the dissociation of the steam, and (ii) combination of the iron with the dissociated oxygen.

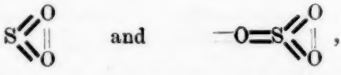
88. **"The constitution of sulphurous, sulphuric, carbonic, and formic acids."** **By John Albert Newton Friend.**

In a recent communication, Miss Smedley (*Trans.*, 1909, **95**, 231) has discussed the constitution of the carboxyl group, and incidentally suggests that carbonic, sulphurous, and sulphuric acids may be represented by the schemes:

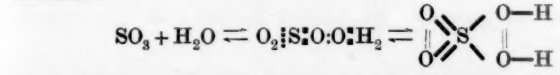


The instability of the first two acids is attributed to the symmetrical arrangement of the third atom of oxygen between two hydroxyl groups.

The present author considers, however, that such an explanation is not sufficient. Arguing along similar lines it would be expected that an acid containing a fourth atom of oxygen between *three* hydroxyl groups would be too unstable to exist, but orthophosphoric acid, $PO(OH)_3$, is comparatively very stable. Evidence has already been adduced (Friend, *Trans.*, 1908, **93**, 266) to show that the molecules of sulphur di- and tri-oxides are most probably correctly represented by the schemes:



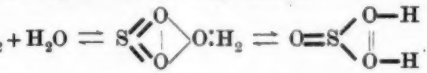
where the thick lines represent the free valencies, and the thin, the latent valencies. Since the latent valencies of the third oxygen atom in the trioxide are unsaturated, the latter readily combines with water to form a stable hydrate, which then undergoes more or less complete rearrangement to sulphuric acid until equilibrium is attained:



Since the hydrate is exceedingly stable, there is little tendency for

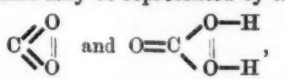
the reactions to proceed from right to left; hence the stability of the sulphuric acid.

With sulphur dioxide, however, the case is different. The latent valencies of the two oxygen atoms mutually saturate each other, and there is little tendency for a hydrate to form; hence equilibrium is obtained according to the following schemes:

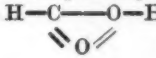


when only a small quantity of the hydrate is present, and the relative concentration of the sulphurous acid can therefore never be great. This would account for the instability of the acid, and the fact that its solution exhibits all the properties of the dioxide. It might appear at first sight that, since sulphur dioxide is unsaturated, a hydrate of the type

might be formed. This is, however, not possible, as the free valencies of the sulphur are positive, whereas one of the latent valencies of the oxygen is positive and the other negative (Friend, *loc. cit.*). Carbon dioxide and carbonic acid may be represented by the schemes:



and a similar explanation for the instability of the acid holds. In formic acid a carboxylic group is present, and the latent valencies of the two oxygen atoms mutually satisfy each other, thus:

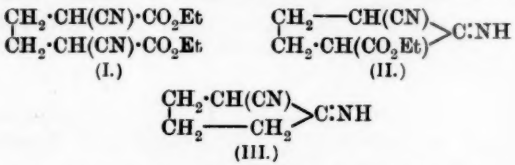


That carbon monoxide does not dissolve in water to form formic acid is explained by the fact that the free and latent valencies of the oxygen atom saturate the four free valencies of the carbon atom, a saturation which is rendered possible by the amphoteric nature of the latter (Friend, *loc. cit.*); hence it is not until some vigorous method is adopted for breaking this connexion, as, for example, the action of the gas on heated potassium hydroxide, that formic acid can be prepared.

89. "The formation and reactions of imino-compounds. Part IX. The formation of derivatives of *cyclo*pentane from αδ-dicyano-derivatives of butane." By Stanley Robert Best and Jocelyn Field Thorpe.

When ethylene dibromide reacts with dry ethyl sodiocyanoacetate (compare this vol., p. 17) in benzene solution, ethyl αδ-dicyanoadipate

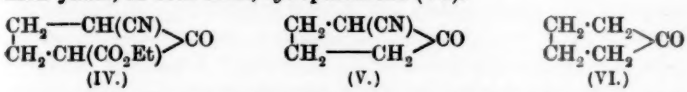
(I) is formed, and this compound is readily transformed into ethyl carbonate and *ethyl* 2-*imino*-3-*cyano*cyclo*pentane*-1-*carboxylate* (II), from which 1-*imino*-2-*cyano*cyclo*pentane* (III) can be easily obtained.



(I.) (II.)

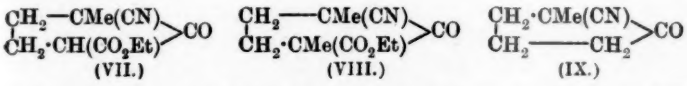
(III.)

These imino-compounds are hydrolysed by cold mineral acids, yielding *ethyl* 5-*cyano*cyclo*pentan*-1-*one*-2-*carboxylate* (IV) and 2-*cyano*-cyclo*pentan*-1-*one* (V) respectively, whilst further treatment with acids yields, in both cases, *cyclo*pentanone (VI).



(IV.) (V.) (VI.)

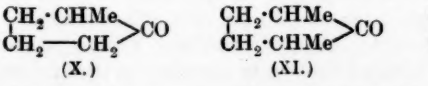
The methylation of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (IV) leads to the formation of *ethyl* 5-*cyano*-5-*methyl*cyclo*pentan*-1-*one*-2-*carboxylate* (VII) and *ethyl* 5-*cyano*-2 : 5-*dimethyl*cyclo*pentan*-1-*one*-2-*carboxylate* (VIII); the first-named compound, on hydrolysis, is transformed into 2-*cyano*-2-*methyl*cyclo*pentan*-1-*one* (IX), which is identical with the compound prepared by the methylation of 2-cyano*cyclo*-pentan-1-one (V).



(VII.) (VIII.) (IX.)

The ethylation of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (II) yields a mixture consisting of four parts of the *O*-ethyl derivative and one part of the *C*-ethyl derivative.

The *cyclo*pentane ring in these compounds is stable towards acid hydrolysing agents, and therefore 2-*methyl*cyclo*pentan*-1-*one* (X), 2 : 5-*dimethyl*cyclo*pentan*-1-*one* (XI), and 2-*ethyl*cyclo*pentan*-1-*one* (XII) can be readily obtained from the compounds mentioned above.

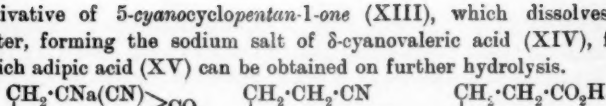


(X.) (XI.) (XII.)

The ring is, however, readily broken by the action of alkalis, the final product in every case being either adipic acid or an alkyl derivative.

Probably the most remarkable instance of the instability of the *cyclo*pentane ring under these conditions is afforded by the sodium

derivative of 5-*cyano*cyclo*pentan*-1-*one* (XIII), which dissolves in water, forming the sodium salt of δ-cyanovaleric acid (XIV), from which adipic acid (XV) can be obtained on further hydrolysis.



(XIII.) (XIV.) (XV.)

90. "The preparation of methyl 1 : 1-dimethyl*cyclo*pentan-3 : 4-dione-2 : 5-dicarboxylate." By Jocelyn Field Thorpe.

Methyl 1 : 1-dimethyl*cyclo*pentan-3 : 4-dione-2 : 5-dicarboxylate, $CMe_2\cdot CH(CO_2Et)$ / $CH(CO_2Et)\text{—}CO$ >CO, was first prepared and identified by Dieckmann (*Ber.*, 1899, **32**, 1934), the method used for its preparation being the interaction of ethyl oxalate and methyl ββ-dimethylglutarate in the presence of sodium ethoxide. Dieckmann prepared this substance with the expressed object (*loc. cit.*, p. 1935) of ultimately obtaining from it by reduction and by methylation and reduction acids of the same formulæ as those proposed by Bredt for camphoric acid and apocamphoric acid, but he remarks (*loc. cit.*, p. 1933) that the yield of the dimethyl salt is exceedingly small.

Dieckmann was evidently unable to overcome the initial difficulties occasioned by this poor yield, as the syntheses proposed by him were ultimately accomplished by Komppa (*Ber.*, 1901, **34**, 2472; 1903, **36**, 4332).

In the first of these papers (*Ber.*, 1901, **34**, 2473), Komppa stated that he had succeeded in obtaining an "almost quantitative yield" of methyl-1 : 1-dimethyl*cyclo*pentan-3 : 4-dione-2 : 5-dicarboxylate from ethyl oxalate and methyl ββ-dimethylglutarate. He omitted to mention, however, either in his paper on apocamphoric acid or on camphoric acid, the conditions under which this increased yield could be obtained.

During the past two years the author has made numerous experiments with the object of reproducing the conditions employed by Komppa, because it was desired to prepare a quantity of this methyl salt for the purposes of another investigation, but in no one of these experiments has the yield exceeded 10 per cent. of the theory.

In view of this difficulty, and of the fact that private communications with Professor Komppa have been unsuccessful in obtaining the details of this important preparation, the author suggests that, as eight years have now elapsed since the publication of Komppa's paper on apocamphoric acid, and six years since he published his preliminary paper on the synthesis of camphoric acid, publication of the full experimental details is highly desirable.

91. "Condensations of cyanohydrins. Part I. Condensation products from anisaldehydecyanohydrin and cinnamaldehydecyanohydrin." By Hamilton McCombie and Ethel Parry.

Minovici (*Ber.*, 1899, **32**, 2206) described the action of dehydrating agents on anisaldehydecyanohydrin as resulting in the production of a compound melting at 146°, to which he assigned the formula $CH_3\cdot O\cdot C_6H_4\cdot CH(CN)\cdot CO\cdot C_6H_4\cdot O\cdot CH_3$. This substance has now been shown to be 2 : 5-di-*p*-methoxydiphenyloxazole,

$$\begin{matrix} N=C(C_6H_4\cdot OMe) \\ | \qquad\qquad \rangle O, \\ CH:C(C_6H_4\cdot OMe) \end{matrix}$$

which was originally described by Minovici himself (*Ber.*, 1896, **29**, 2100), and its formation in this reaction is due to the presence of unchanged aldehyde in the cyanohydrin.

When pure anisaldehydecyanohydrin is subjected to the action of gaseous hydrogen chloride, two substances are formed, namely : (1) a compound melting at 156°, the constitution of which is to be more fully investigated, and (2) *3-keto-2 : 5-di-*p*-methoxydiphenyl-3 : 4-dihydro-1 : 4-diazine*, $N\begin{matrix} C(C_6H_4\cdot OMe)\cdot CO \\ \rangle NH \\ CH:C(C_6H_4\cdot OMe) \end{matrix}$ (compare Japp and Knox, Trans., 1905, **87**, 701).

Cinnamaldehydecyanohydrin, on being subjected to the action of gaseous hydrogen chloride, yields *3-keto-2 : 5-distyryl-3 : 4-dihydro-1 : 4-diazine*.

92. "Labile isomerism among the acylsalicylamide, acylhydroxyamine, and phenylbenzometoxazine groups." By Arthur Walsh Titherley and William Longton Hicks.

In order to throw fresh light on the mechanism underlying the wandering of acyl groups in derivatives of salicylamide and aromatic *o*-hydroxyamines, the behaviour of phenylbenzometoxazone with phosphorus pentachloride has been studied; and evidence has been obtained that the resulting 2 : 4-dichlorophenylbenzometoxazine under the influence of phosphoryl chloride exhibits tautomeric behaviour owing to wandering of chlorine atoms, thus :

$$C_6H_4\begin{matrix} CCl:N\cdot CCl_2Ph \\ O\cdot POCl_2 \end{matrix} \quad (A.) \quad \rightleftharpoons \quad C_6H_4\begin{matrix} CCl:N \\ O\text{—}CClPh \end{matrix} + POCl_3 \rightleftharpoons$$

$$C_6H_4\begin{matrix} CCl:N\cdot POCl_2 \\ O\cdot CCl_2Ph \end{matrix} \quad (B.) \quad .$$

A bright yellow, crystalline substance is obtained which is decomposed by water, yielding benzoylsalicylonitrile, but by 98 per cent.

sulphuric acid yielding *N*-benzoylsalicylamide. As the same yellow solid is produced by the action of phosphorus pentachloride on benzoylsalicylonitrile, it must be regarded either as a mixture of *A* and *B*, or one of these in a labile form.

In the production of the yellow substance from phenylbenzometoxazone, various by-products are obtained, among which the double compound of phosphoryl chloride and 4-chlorophenylbenzometoxazine, $C_6H_4<^{CCl:N}_{O---CHPh}$, appears to be present. Benzylidene chloride is also produced in considerable quantity together with chlorophosphorus derivatives of salicylonitrile.

93. "The alkyl compounds of platinum." By William Jackson Pope and Stanley John Peachey.

The authors have continued the investigation of the salts derived from trimethylplatinic hydroxide, $(CH_3)_3Pt{\cdot}OH$, concerning which they have already published a preliminary note (*Proc.*, 1907, **23**, 86).

94. "Note on the preparation of trimethyl*cyclo*hexenone (*iso*phorone) from ethyl malonate and chlorodimethyl*cyclo*hexenone." By Arthur William Crossley and Charles Gilling.

In a recent communication (*Trans.*, 1909, **95**, 20) it has been shown that when the sodium compound of ethyl malonate acts on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one, the condensation product does not consist of the substance having formula I, as might have been expected, but of ethyl 1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one-5-acetate (II). The formation of this latter compound necessitates the elimination of a carbethoxy-group, and it has now been proved that the reaction affords another instance of the production of ethyl carbonate during such condensations:

$$CMe_2<^{CH_2\cdot CO}_{CH_2---C}>CH \quad \text{(I.)} \quad CH(CO_2Et)_2 + EtOH =$$

$$CMe_2<^{CH_2\cdot CO}_{CH_2---C}>CH \quad \text{(II.)} \quad CH_2\cdot CO_2Et + CO(OEt)_2$$

(compare Thorpe, *Trans.*, 1905, **87**, 1681; also *Proc.*, 1909, **25**, 17; Leuchs and Geserick, *Ber.*, 1908, **41**, 4171).

Twenty-four grams of chlorodimethyl*cyclo*hexenone were treated with ethyl malonate as already described (*loc. cit.*, p. 23). The steam

distillate was extracted with ether, the ethereal solution dried, evaporated, and the residual 28 grams of liquid fractionally distilled, using a colonna. After three distillations, 7·5 grams of a liquid with an ethereal odour were obtained, boiling constantly at 126°, and giving the following numbers on analysis :

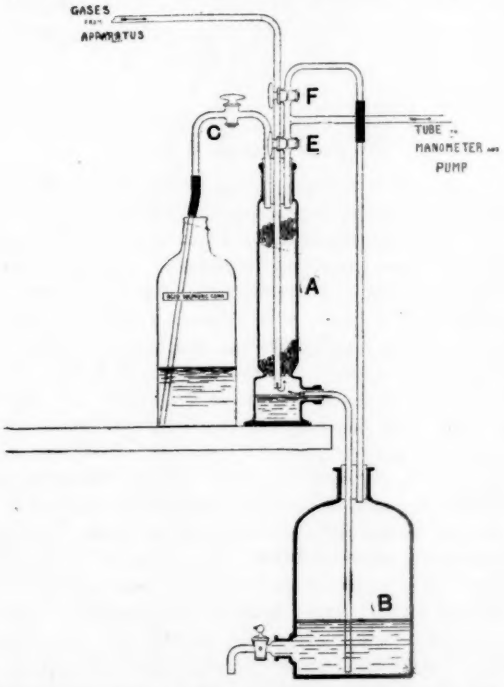
0·1927 gave 0·3575 CO_2 and 0·1471 H_2O. C = 50·59 ; H = 8·48.

$C_5H_{10}O_3$ requires C = 50·84 ; H = 8·47 per cent.

These data prove the substance to be ethyl carbonate.

95. "A simple gas-drying apparatus for use with a mechanical exhaust pump." By George Stanley Walpole.

It is found convenient in chemical laboratories to use a mechanical exhaust pump for many purposes, especially in conjunction with



distillation apparatus. To maintain the pump in such a condition that at any moment it is capable of working at its maximum efficiency, it must be kept dry by use of either a steam-jacket or else an efficient drying apparatus interposed between it and the still.

The accompanying drawing represents a form of desiccator which has been in use continuously for some months under somewhat severe conditions.

The gases from the still pass directly down the tower *A*. If the tap *E* be closed and *F* open, they pass through the concentrated sulphuric acid in the reservoir *B*. This is the arrangement when the still is being exhausted at the commencement of distillation or when only a moderate vacuum is required. If the tap *F* is closed and *E* opened, the gases pass up the tower, meeting a slow stream of sulphuric acid running over the glass beads and regulated by tap *C*.

In this arrangement a short circuit is thus established which eliminates the hydrostatic pressure of the sulphuric acid in the bottle *B*, and there is no resistance offered to the gases passing to the pump. It is advisable to leave all taps turned off when the apparatus is not in use. The acid from *B* can be run out periodically, and if suitable, used again.

96. "Some esters of antimony trioxide."
By John Francis MacKey.

Lang, MacKey, and Gortner (*Trans.*, 1908, **93**, 1364) described a new method for the esterification of arsenious oxide with the aliphatic alcohols and with phenol and its homologues, and expressed the opinion that similar esters might be obtained from antimony trioxide and the same alcohols and phenols. In the present work attempts have been made to form these esters by treating a mixture of antimony trioxide and the alcohol or phenol in the following ways: (1) heating under a reflux condenser; (2) heating with Soxhlet attachment and anhydrous copper sulphate; (3) heating in sealed tubes at 150°; (4) heating with metallic calcium; (5) treating with anhydrous copper sulphate in the cold. By the second method, yields of from 3 per cent. in the case of ethyl antimonite to 15 per cent. in the case of *iso*butyl antimonite, and of 40 per cent. in the case of phenyl antimonite to 48 per cent. in the case of *m*-tolyl antimonite, were obtained. By heating with metallic calcium a yield of 60 per cent. was obtained with phenyl antimonite. The following esters were isolated in quantity: *methyl*, *ethyl*, *propyl*, iso*butyl*, *amyl*, iso*amyl*, *phenyl* o-, m- and p-*tolyl antimonites*. The aliphatic esters are all liquids, which decompose on heating at atmospheric pressure into antimony trioxide and the alcohol from which they were prepared, whilst phenyl, *o*-tolyl, and *p*-tolyl antimonites are solids melting at 13°, 16°, and 14° respectively. The boiling points of these esters, under 30 mm. pressure, are as follows: methyl, 65°; ethyl, 115—120°; propyl, 143°; *iso*butyl, 144°;

amyl, 170°; *iso*amyl, 163°; phenyl, 250°; *o*-tolyl, 352°; *m*-tolyl, 300°; and *p*-tolyl, 345°. They are soluble in absolute alcohol, ether, chloroform, or benzene, but decompose immediately on the addition of water into antimony trioxide and the alcohol from which they were prepared. Accurate methods of analysis have been worked out for both the esters of the aliphatic alcohols and the esters of phenol and its homologues. On analysis these esters were found to correspond with the general formula R_3SbO_3.

ADDITIONS TO THE LIBRARY.

THE FOLLOWING BOOKS HAVE BEEN PRESENTED TO THE LIBRARY BY Mr. EDWARD DAVIES.

Boyle, *Robert.* Opera varia, quorum posthac exstat catalogus. Cum indicibus necessariis, multisque figuris æneis. Genevæ 1680. 12 parts. (2 copies, 1 wanting portrait.)

—— Experimentorum novorum physico-mechanicorum continuatio secunda, *etc.* pp. viii + 132. ill. Genevæ 1682. (2 copies.)

—— Apparatus ad historiam naturalem sanguinis humani, ac spiritus præcipue ejusdem liquoris. pp. viii + 47. Genevæ 1686.

—— Observationes de Salsedine Maris. pp. 23. Genevæ 1686.

—— Tentamen porologicum sive ad porositatem corporum tum animalium, tum solidorum detegendam. pp. vi + 46. Genevæ 1686.

—— De specificorum remediorum cum corpusculari philosophia concordia, *etc.* pp. viii + 64. Genevæ 1687.

—— Tractatus de ipsa natura, *etc.* pp. xvi + 111. Genevæ 1688.

—— Origo formarum et qualitatum juxta philosophiam corpuscularem, *etc.* pp. xxxii + 147. Genevæ 1688.

—— Noctiluca aeria sive nova qúædam phænomena in substantiæ factitiæ sive artificialis, Sponte Lucidæ, productione observata, *etc.* pp. 108. Genevæ 1693.

—— Summa veneratio Deo ab humano intellectu debita, *etc.* pp. 43. Genevæ 1693.

—— Medicina hydrostatica, sive hydrostatica materiæ medicæ applicata, *etc.* pp. xii + 70. Coloniæ Allobrogum 1693.

—— De amore seraphico seu de quibusdam ad Dei amorem stimulis pp. viii + 59. Genevæ 1693.

—— Experimenta nec non observationes circa variarum particularium qualitatum originem, sive productionem mechanicam: Quibus accesserunt tractatus quo imperfecta chymistarum doctrina de

qualitatibus detegitur, & quædam in hypothesin de alcali & acido animadversiones. pp. xvi + 144. Genevæ 1694.

—— Exercitationes circa utilitatem philosophiæ naturalis experimentalis, *etc.* pp. xvi + 602. Genevæ 1694.

—— Novorum experimentorum physico-mechanicorum continuatio prima, *etc.* pp. xii + 123. ill. Genevæ 1694.

—— Experimenta et notæ circa producibilitatem chymicorum principiorum: Quæ sunt totidem partes appendicis ad Scepticum Chymicum. pp. xii + 92. Genevæ 1694.

—— Examen dialogi physici domini T. Hobbs, de natura aëris, *etc.* pp. viii + 67. Genevæ 1695.

—— Tractatus varii continentes nova experimenta circa relationem inter flammam & aerem et circa explosiones, *etc.* pp. iv + 120. Genevæ 1696.

—— Generalia capita pro historia naturali regionum majorum vel minorum, *etc.* pp. iv + 39. Genevæ 1696.

—— Excellentia theologiæ cum naturali philosophia, *etc.* pp. viii + 87. Genevæ 1696.

At the next Ordinary Meeting on **Thursday**, April **1st**, 1909, at 8.30 p.m., the following papers will be communicated:

"The affinity values of certain alkaloids." By V. H. Veley.

"The preparation and properties of the *N*-tribromo-substituted hydrazines usually styled the diazoperbromides." By F. D. Chattaway.

"The coloured salts and derivatives of the thiovioluric acid group." Preliminary note. By P. C. C. Isherwood.

"Nitrosoacetylamino-derivatives of the benzene and diphenyl series." By J. C. Cain.

"Observations on phycoerythrin, the pigment of the red algæ." By E. K. Hanson.

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Issued 29/4/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 355.

Thursday, March 25th, 1909, Annual General Meeting, SIR WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Dr. G. BARGER and Mr. W. B. TUCK were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society during the past twelve months, and the Treasurer, after making a statement as to the Society's income and expenditure for the year 1908, proposed a vote of thanks to the Auditors, which was seconded by Dr. H. G. COLMAN and acknowledged by Dr. A. HARDEN and Dr. V. H. VELEY.

The adoption of the Report of Council together with the Balance Sheet and Statements of Accounts for the year ended 31st December, 1908, was proposed by Prof. J. NORMAN COLLIE, and seconded by Mr. JOHN SPILLER. After some remarks by Dr. E. DIVERS, the motion was put to the Meeting and carried unanimously.

REPORT OF THE COUNCIL.

The Council once more have the satisfaction of stating that the prosperity of the Society continues, both the number of papers read and the number of Fellows on the list showing a considerable increase.

On the 31st December, 1907, the number of Fellows was 2,896. During 1908, 159 Fellows were elected, and 4 were reinstated, thus making a gross total of 3,059. The Society has lost 31 Fellows by death; 38 have resigned; 2 elections have become void, and the names of 38 Fellows have been removed from the list for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at the 31st December, 1908, was 2,950, showing an increase of 54 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:

J. H. Ball (1902).
S. Banner (1888).
B. H. Brough (1884).
J. T. Cart (1907).
A. V. Cunnington (1898).
A. Deck (1874).
Sir J. Evans (1876).
E. A. Fasnacht (1902).
R. J. Friswell (1871).
Sir J. C. Gamble (1876).
T. A. Gerard (1904).
W. M. Habirshaw (1874).
R. H. Harland (1876).
F. W. Hart (1869).
A. Helms (1894).
A. Houldershaw (1901).
R. V. Jackson (1881).
J. G. Johnson (1872).
W. H. Jowett (1891).
F. H. Leeds (1891).
T. Morson (1851).
H. L. Pendlebury (1907).
J. H. Player (1860).
W. A. Shenstone (1876).
A. Sibson (1859).
F. G. Smith (1903).
E. Sonstadt (1874).
Sir T. Stevenson (1864).
B. H. Thwaite (1880).
A. Wade (1908).
T. H. Walker (1879).

The following Fellows have resigned:

J. Alexander.
J. A. Basker.
F. W. Bayly.
J. H. Belcher.
L. H. Berry.
W. R. Cooper.
A. J. Cownley.
D. C. Crichton.
C. Crocker.
F. W. Daw.
F. A. Drake.
L. Dufty.
G. C. Fry.
T. Gough.
A. H. Green.
H. L. Greville.
E. G. Guest.
C. G. Kiddell.
W. J. Lockyer.
J. Marsh.
L. W. Mathieson.
E. W. Millar.
E. Morris.
W. D. Page.
H. Ross.
H. Rostron.
H. Senier.
F. Shedden.
E. C. Sherwood.
E. S. Smith.
W. Southworth.
A. Turner.
G. J. Ward.
R. Waterhouse.
T. Whittaker.
W. H. Wood.
J. W. Yates.

and Professor A. Haller, whose name has been transferred from the list of Ordinary Fellows to that of the Honorary and Foreign Members.

The number of those Fellows elected prior to 1860 has been diminished by the death of Mr. Thomas Morson, elected on December 15th, 1851, and of Mr. Alfred Sibson, who was elected on December 15th, 1859.

The Council have great pleasure in congratulating Professor William Odling and Mr. E. A. Pontifex on having reached the 60th Anniversary of their Election as Fellows of the Society; the following Fellows during the past two or three years have reached their Jubilee as Fellows:

Prof. A. H. Church (1856).	Mr. C. Hanbury (1857).
Sir W. Crookes (1857).	Prof. J. W. Mallet (1857).
Mr. E. Davies (1858).	Mr. F. Norton (1854).
Mr. J. F. Davis (1857).	Sir H. E. Roscoe (1855).
Prof. G. Carey Foster (1856).	Mr. P. J. Worsley (1858).

The number of Honorary and Foreign Members at the close of 1907 was 29. Seven were elected in February, 1908, but during the past year the Society has had to mourn the death of Professor A. H. Becquerel and of Professor Wolcott Gibbs, thus making the total of Honorary and Foreign Members, at the close of 1908, to be 34. Since then, however, Professor Emil Erlenmeyer and Professor Julius Thomsen, F.R.S., have passed away. Arrangements are being made for the preparation of Memorial Lectures, and that dealing with the life work of Professor Wolcott Gibbs will be delivered by Dr. Frank Wigglesworth Clarke early in June.

A general scheme of co-operation with the Royal Society in the matter of Obituary Notices has been formulated; it will now be possible to issue those relating to deceased Fellows in the publications of both Societies, subject to the consent of the author.

During the year 1908, 278 scientific communications have been made to the Society, 212 of which have been published already in the Transactions, and abstracts of all have appeared in the Proceedings.

The volume of Transactions for 1908 contains 2,281 pages, of which 2,188 are occupied by 222 memoirs, the remaining 93 pages being devoted to the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 205 memoirs, which occupy 2,021 pages.

The Journal for 1908 contains also 4,978 abstracts of papers published mainly in foreign journals, which extend to 2,112 pages,

whilst the abstracts for 1907 numbered 4,686, and occupied 2,100 pages. The abstracts for 1908 may be classified as follows :—

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	1,032	1,879

PART II.

General and Physical Chemistry		936
Inorganic Chemistry		588
Mineralogical Chemistry		97
Physiological Chemistry		567
Chemistry of Vegetable Physiology and Agriculture		265
Analytical Chemistry		646
	1,080	3,099
Total in Parts I. and II.	2,112	4,978

In July, 1908, the Linnean Society celebrated the fiftieth anniversary of the presentation, by C. R. Darwin and A. R. Wallace, of the essay entitled "On the tendency of species to form varieties, and on the perpetuation of varieties and species by natural means of selection"; on this occasion the Chemical Society was represented by the Foreign Secretary, Dr. Horace T. Brown. Another jubilee of especial interest, held in October, was that of the Foundation of the Oxford University Museum, which followed upon the establishment of a Natural Science School at Oxford; at this ceremony the President, Sir William Ramsay, offered to the University the congratulations of the Society.

Late in 1907, the President was nominated on the deputation organised by the British Science Guild, which subsequently represented to the Postmaster-General the desirability of reducing postage rates for the publications of learned Societies; this deputation was received by the Postmaster-General on March 12th, 1908, but his reply was not sympathetic. Following this action, a memorandum on the subject was prepared, and forwarded to certain members of Parliament, some of whom communicated in the matter with the official representatives of the Post Office in the House; the majority of these members, however, were of opinion that it is undesirable to raise this question again at present.

The Society has become indebted to Professor J. Emerson Reynolds for a bust of Michael Faraday.

In May, 1908, a petition, signed by more than three hundred

Fellows, was presented to the Council requesting them to ascertain the wishes of the Society as a whole regarding the admission of women to the Fellowship of the Society. Acceding to the request of the memorialists, the Council directed the Secretaries to issue a letter, drawn up by the Council, in which arguments on both sides were set forth, requesting each Fellow to consider these, and to express his opinion on the ballot paper enclosed therewith. The referendum having closed on October 1st, the scrutators reported that 1,758 voting papers had been received, of which 1,094 were in favour of admitting women, and 642 against the proposal, whilst 22 were neutral. Two Extraordinary Meetings of Council were devoted solely to the consideration of this result, and it was resolved, by a considerable majority, "That in the opinion of this Council it is desirable that at any time, on recommendation of three Fellows of the Society, women be accepted as Subscribers to the Society. Such women Subscribers shall pay an annual fee of thirty shillings: they shall be admitted to all ordinary meetings of the Society: they shall have the same use of the Library as the Fellows, and they shall be supplied with the Proceedings, Transactions, and Annual Reports of the Society as these are issued." The considerations which led the Council to adopt this course are set forth in the statement drawn up by the Council and made by the President at the Ordinary Scientific Meeting on December 17th, 1908 (*Proceedings*, 1908, **24**, 277).

The validity of this resolution having been called in question (*Proceedings*, 1909, **25**, 1), the terms of the resolution and of the criticisms thereon were referred to the legal advisers of the Society, Messrs. Bristows, Cooke and Carpmael, who report as follows:

"In our opinion, the Council had power to pass this resolution. The privileges thereby proposed to be given do not in any way make women subscribers Corporators, and it was because if women were elected Fellows they would become Corporators, that Counsel, in April, 1904, advised they should not be elected Fellows.

"(1) So far as we are aware (taking the parts of the Resolution one by one), there is nothing to prevent women subscribing an annual fee to the Society, or to prevent the Society accepting such fee. Gifts are from time to time made to the Society. The Charter provides that the Council shall have the sole management of the income and Funds of the Society.

"(2) The Resolution also provides that women shall be admitted to all ordinary meetings of the Society. We understand that this has always been the custom.

"(3) The Resolution next provides that the women shall have the same use of the Library as the Fellows. So far as we are aware,

there is nothing in the Charter or By-Laws to prevent this, but if it is proposed that the books shall be allowed to circulate among the women Subscribers, then we think that By-Law 15 would have to be altered.

"(4) Lastly, the Resolution provides that women subscribers shall be supplied with the Proceedings, Transactions, and Annual Reports of the Society as these are issued. We see nothing contrary to the Charter or By-Laws in this, and, further, we understand that any member of the public at present has this facility at prices fixed by the Council."

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote Chemical Science by Research, was made, on the recommendation of the Research Fund Committee, to Professor Frederic Stanley Kipping, F.R.S. The medal will be presented at the Annual General Meeting on March 25th, 1909.

The Council have regretfully accepted the resignation of Mrs. Dougal. A special vote of thanks has been accorded to Mrs. Dougal in recognition of the valuable assistance which she has rendered to the Society during the past fifteen years in indexing its Publications. Dr. C. H. Desch having resigned the position of Assistant Sub-Editor, an arrangement has been made by which all branches of the editorial work will become concentrated in the hands of Dr. Cain and Mr. Greenaway.

Following the important gift of books by Sir Henry Roscoe mentioned in the Report of the Council for 1906, the munificence of the same donor has enriched the Library with a series of periodicals comprising 636 volumes. The Society is indebted also to Mrs. Sonstadt, Mr. Edward Davies, and Professor W. R. E. Hodgkinson, for the gift of valuable sets of books.

The number of books borrowed from the Library during 1908 was 1,339 as against 1,317 in the previous year. The additions to the Library, excluding those already mentioned, comprise 159 books, of which 90 were presented, 412 volumes of periodicals (representing 245 journals), and 36 pamphlets, as against 138 books, 401 volumes of periodicals (representing 243 journals), and 40 pamphlets last year.

In further response to the appeal of the Council referred to in the Report of last year, several Fellows have presented volumes of periodicals to help to complete the sets in the Library. The appeal has also stimulated Fellows to present to the Library a number of early chemical works. The Council welcome gifts of this description, as, in the words of Professor Emerson Reynolds, speaking from the Presidential Chair in 1902, "it is desirable that the Society should

have in the Library one copy, at least, of every work printed in English on chemical subjects to the end of the eighteenth century." Each of these gifts has been acknowledged in the Proceedings from time to time.

In consequence of the crowded condition of the Library, it has been again found necessary to construct ten bookcases in the basement; this extension, however, can afford only temporary relief.

The annual income of the Research Fund now amounts to about £346, and this year, as a fair balance was also in hand, grants amounting to £368 were made. In the Transactions for 1908, there are 31 papers contributed by authors who have received grants from the Research Fund.

With regard to the income and expenditure of the Society for the year just closed, there is but little calling for special comment, as both are on the same lines as those of last year. The total income for 1908 is £7,134 17*s.* 2*d.*, which is less than that of the previous year by £125 7*s.* 8*d.*; the expenditure is £6,834 15*s.*, or only £84 6*s.* 7*d.* more than that of last year. This leaves an excess of £300 2*s.* 2*d.* of income over expenditure for the year's working, as compared with £509 16*s.* 5*d.* for 1907, and £741 13*s.* 2*d.* for 1906. It may seem somewhat remarkable that, with an increase of 50 in our list of Fellows, we should have a smaller income from admission fees and from annual subscriptions, which are the items in which there is the most notable falling off. This is, however, accounted for by the large number elected in November and December, whose subscriptions and admission fees do not become due until January 1st, 1909, and therefore do not appear as arrears in the 1908 account, but will swell the income for 1909. This will be welcome to the Treasurer, for the preparation for Vol. V. of the Decennial Index (which has even now begun) must be actively proceeded with by our Editor under the arrangements just included. The *Journal* has cost £192 2*s.* 6*d.* more than last year, but a saving of £37 15*s.* 6*d.* has been effected on the *Proceedings*. Administrative expenses are £54 5*s.* 4*d.* less than last year, due to our economies in several directions being greater than increased expenditure in others, but the total effect has been to secure greater efficiency. It is obvious, however, that unless authors will actively aid the Publication Committee in their endeavours to keep down the continual increase in the cost of the *Journal*, it will be necessary to raise the annual subscription from £2 (which it has been ever since the foundation of the Society) to £2 10*s.*

Dr. DIVERS having given due notice that he would move the adoption of the following new Bye-Law:

XIII *bis.—On Ascertaining the Will of the Society by means of Voting Papers.*

> "The President, either on his own motion or on a written requisition by the Council or by fifty Fellows, shall proceed to ascertain the will of the Society as to any suggested change in the Bye-Laws or in the administration of these laws by the Council, by causing to be delivered, along with the Proceedings or separately, a notice to each Fellow of the change proposed, together with a voting paper upon it, to be filled in by the Fellow and returned to the Secretaries not later than a prescribed date. After that date, the results of the voting shall be counted by the Secretaries and two Scrutineers, appointed by the President, and be reported by him to a Council Meeting and to a General Meeting, upon which the Council shall proceed to act in accordance with the majority of votes, as being the expression of the will of the majority,"

the President declared that his duty prevented him from putting the proposition to the Meeting, the suggested Bye-Law being repugnant to the Charter. Dr. DIVERS then withdrew his Resolution, and gave notice that at a subsequent General Meeting he would propose the Bye-Law so amended that the word "may" replace the word "shall."

The PRESIDENT then presented the Longstaff Medal for 1909 to Professor F. S. KIPPING, who responded in terms expressing his appreciation of the honour bestowed upon him.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary and Council for their services during the past year was proposed by Dr. L. T. THORNE, seconded by Dr. MCGOWAN, and acknowledged by Prof. H. E. ARMSTRONG.

The PRESIDENT then delivered his address, entitled "Elements and Electrons." Prof. J. J. DOBBIE proposed a vote of thanks to the President coupled with the request that he would allow his address to be printed in the Society's Transactions, the motion being seconded by Prof. F. S. KIPPING, and acknowledged by the PRESIDENT.

The Scrutators having presented their report, the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year.

President: Harold B. Dixon, M.A., F.R.S.

Vice-Presidents who have filled the Office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A.,

LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents: J. Campbell Brown, D.Sc., LL.D.; J. Norman Collie, Ph.D., F.R.S.; J. J. Dobbie, M.A., D.Sc., F.R.S.; F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; James Walker, D.Sc., Ph.D., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc. Ph.D., F.R.S.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: Julian L. Baker; George T. Beilby, F.R.S.; William A. Bone, D.Sc., Ph.D., F.R.S.; Alfred C. Chapman; Julius B. Cohen, Ph.D., B.Sc.; Charles E. Groves, F.R.S.; J. T. Hewitt, M.A., D.Sc., Ph.D.; W. R. E. Hodgkinson, Ph.D.; H. R. Le Sueur, D.Sc.; G. T. Morgan, D.Sc.; A. G. Perkin, F.R.S.; A. E. H. Tutton, M.A., D.Sc., F.R.S.

ANNIVERSARY DINNER.

The Anniversary Dinner of the Society was held at the Whitehall Rooms, Hotel Metropole, on Thursday, March 25th, 1909, at 7 p.m., at which the following Guests and Fellows were present:

Applebey, Mr. M. P.
Armit, Dr. H.
Baker, Mr. J. L.
Balfour of Burleigh, Rt. Hon. Lord, *Chancellor, St. Andrews University.*
Barclay, Mr. E., *President, Institute of Brewing.*
Barger, Dr. G.
Barrett, Mr. W. H.
Barry, Sir J. Wolfe-, *Chairman, Executive Committee, City and Guilds of London Institute.*
Beadle, Mr. C.
Bell, Sir Hugh, *President, Iron and Steel Institute.*
Bemcastle, Mr. R.
Bevan, Mr. E. J.
Borns, Dr. H.
Bovey, Dr. H. T., *Rector, Imperial College of Science and Technology.*
Bowley, Mr. J. J.
Brown, Prof. A. J.
Cain, Dr. J. C., *Editor.*
Carr, Mr. S. E., *Assistant Secretary.*
Chapman, Mr. A. C.
Cholmeley, Dr. H. P.
Chree, Dr. C., *President, Physical Society.*
Clifford, Mr. F. W., *Librarian.*
Collins, Sir William J., *Vice-Chancellor, London University.*
Colman, Dr. H. G.
Connah, Mr. J.
Cozens-Hardy, Rt. Hon. Sir H. H., *Master of the Rolls.*
Crichton-Browne, Sir James, *Treasurer, Royal Institution.*
Crookes, Sir William, *Past President.*
Crossley, Prof. A. W., *Hon. Secretary.*
Daily Telegraph, The.
Dale, Dr. H. H.
Divers, Prof. E.
Dobbie, Prof. J. J., *Vice-President.*
Dyer, Dr. B.
Edwards, Mr. S. A.
Elborne, Mr. W.

Elder, Mr. H. M.
Evans, Mr. P. M., *Clerk, Clothworkers' Co.*
Exeter, Rt. Rev. Lord Bishop of.
Feilmann, Dr. M. E.
Fenton, Dr. H. J. H.
Forster, Dr. M. O., *Hon. Secretary.*
Gardner, Mr. W. S., *Master, Drapers' Co.*
Geikie, Sir Archibald, *President, Royal Society.*
Goodenough, Mr. F. W.
Greenaway, Mr. A. J., *Sub-Editor.*
Griffiths, Mr. T. P., *Prime Warden, Dyers Co.*
Gwyer, Dr. A. G. C.
Harden, Dr. A.
Harker, Dr. G.
Hartley, Mr. H.
Hewitt, Dr. J. T.
Hill, Mr. C. A.
Hodgkinson, Prof. W. R. E.
Holt, Mr. A.
Hooper, Mr. E. G.
Howard, Mr. D.
Huntley, Mr. G. N.
Jowett, Dr. H. A. D.
Keeble, Mr. A. J.
Keeble, Mr. H.
Kemp, Mr. W. J.
Kipping, Prof. F. S., *Vice-President.*
Lapworth, Dr. A.
Lessing, Dr. R.
Le Sueur, Dr. H. R.
Little, Dr. G.
Lockyer, Sir J. Norman, *Chairman, British Science Guild.*
Lowry, Dr. T. M.
Macdonald, Prof. J. S.
MacEwan, Mr. P.
McGowan, Dr. G.
Maltwood, Mr. J.
Matthews, Dr. F. E.
Meldola, Prof. R., *President, Society of Chemical Industry.*
Messery, Mr. G. T.
Metcalfe, Mr. F. E.
Miers, Dr. H. A., *Principal, London University.*
Mills, Dr. W. H.
Mohr, Dr. B.
Mondy, Mr. E. F.
Moody, Dr. G. T.
Morant, Sir Robert L., *Permanent Secretary, Board of Education.*
Morgan, Dr. G. T.
Morning Post, The.
Morrell, Dr. R. S.
Morris, Mr. H., *President, Royal College of Surgeons.*
Müller, Dr. H., *Past President.*
Murphy, Mr. P.
Ogilvie, Mr. F. G., *Principal Assist.-Sec., Board of Education.*
Orton, Prof. K. J. P.
Pearson, Mr. G. E.
Perkin, Prof. W. H., *Vice-President.*
Ping, Mr. W.
Pope, Prof. W. J.
Power, Dr. F. B.
Prain, Lt.-Col. D., *Director, Kew Gardens.*
Press Association, The.
Prideaux, Sir W. S., *Clerk, Goldsmiths' Co.*
Ramsay, Sir William, *President.*
Ramsay, Mr. W. G.
Reay, Rt. Hon. Lord, *Chairman, University College.*
Reynolds, Prof J. E., *Past President.*
Roberts, Mr. F. A., *Master, Grocers' Co.*
Russell, Dr. W. J., *Past President.*
Scott, Dr. A., *Treasurer.*
Scott, Dr. D. H., *President, Linnean Society.*
Scudder, Mr. F.
Sidgwick, Dr. N. V.
Spielmann, Dr. P. E.
Standard, The.
Steward, Mr. H. A., *Master, Skinners' Co.*
Struthers, Dr. John, *Secretary, Scotch Education Dept.*
Tatlock, Mr. R. R., *President, Society of Public Analysts.*
Thomas, Mr. N. G.
Thorpe, Dr. J. F.
Tidy, Dr. H. L.
Tilley, Mr. J. W.
Tilley, Mr. V. J.
Times, The.
Tizard, Mr. H. T.
Townshend, Col. G. R.
Vasey, Mr. S. A.
Veley, Dr. V. H.
Voelcker, Dr. J. A.
Warren, Mr. T. H., *Vice-Chancellor, Oxford University.*
White, Sir Wm. H., *Vice-President, Society of Arts.*
Williams, Rt. Hon. Sir Roland Vaughan, *Lord Justice of Appeal.*
Winstanley, Mr. H., *Master, Cloth-workers' Co.*
Wissler, Mr. F.
Wood, Sir H. Trueman, *Secretary, Society of Arts.*
Yates, Mr. H. J.
Young, Dr. G.
Young, Mr. J. Rymer, *President, Pharmaceutical Society.*

The following Toasts were proposed :

By THE PRESIDENT.

1. **His Most Gracious Majesty the King.**
2. **Her Majesty the Queen Alexandra, their Royal Highnesses the Prince and Princess of Wales, and the other Members of the Royal Family.**

By SIR HUGH BELL, Bart.,

President of the Iron and Steel Institute.

3. **The Chemical Society,** coupled with the name of *The President.*

By Professor RAPHAEL MELDOLA, F.R.S.,

Past President of the Chemical Society.

4. **The City and Guilds of London,** coupled with the names of F. A. ROBERTS, Esquire, *Master of the Worshipful Company of Grocers,* and WALTER S. GARDNER, Esquire, *Master of the Worshipful Company of Drapers.*

By Professor H. A. MIERS, F.R.S.,

Principal of the University of London.

5. **Scientific Societies,** coupled with the name of SIR ARCHIBALD GEIKIE, K.C.B., F.R.S., *President of the Royal Society.*

By Professor J. EMERSON REYNOLDS, F.R.S.,

Past President of the Chemical Society.

6. **The Guests,** coupled with the names of The Right Honourable LORD BALFOUR OF BURLEIGH, K.T., P.C., *Chancellor of the University of St. Andrews,* and SIR JAMES CRICHTON-BROWNE, F.R.S., *Treasurer of the Royal Institution.*

The Royal Toasts having been duly honoured, Sir Hugh Bell, Bart., President of the Iron and Steel Institute, in proposing The Chemical Society, coupled with the name of The President, said that no branch of human industry owed a greater debt to the science which that Society had been formed to promote than the Iron and Steel Trade. In every branch of that industry, chemical science was continually assisting, and without it they would be unable to conduct those intricate operations which resulted in such a large measure of well-being to the human family. Even to battleships, of which so much had been heard of late, the President had contributed not a little, but he, Sir Hugh, preferred to emphasise the peaceful side of their industry, and their gratitude to Chemistry and the President of the Chemical Society was rather for having promoted peace, not warfare. It was a science which, if properly used, might be largely instrumental in the education of the youth of our country. Of all the sciences, Chemistry was that one which compassed most completely the true objects of experimental science, seeking always for its verification the repetition of the phenomena under investigation. It too frequently happened, however, that what was called chemical instruction was merely a "messing about" with test-tubes which did no good to any living soul. If it were indeed necessary to exclude all test-tubes from technical departments—even if they had thereby to exclude Chemistry itself—they might be doing something of real benefit to education.

Sir William Ramsay, in responding to the toast, reviewed in an interesting manner the chief events associated with the Society since his entrance into the Society in 1873. He gave a number of interesting and amusing reminiscences of many of the pioneers of modern science with whom he had come into personal contact. Alluding to the inutility of examinations in testing the ability of chemists, he regarded such examinations in the light of a necessary evil. They were inadequate to gauge the abilities of a chemist, which depended upon other mental qualities than readiness, quick-wittedness, and good memory. The latter were undoubtedly useful qualities, but what the chemist more particularly required was the power to obtain accurate results by means of long-continued thought and careful observation. The Chemical Society was expanding in its influence at home and abroad, and had now nearly 3,000 Fellows, and had children and grandchildren in the form of chemical societies practically everywhere, but more especially in the Colonies and the United States. He could not venture to predict what the future of Chemistry might be. The days of the Admirable Crichton were gone, and it was now impossible to be proficient in all branches of human knowledge. It was therefore more necessary than ever that the chemist should know

something about everything in Chemistry, and everything about some particular branch of it. There was an overwhelming output of chemical knowledge, and it was hopeless to attempt to read all the books published nowadays. His advice to authors of works on Chemistry was to reduce them to the irreducible minimum, taking care to be lucid, concise, and sufficiently comprehensive. One aim of the Society should be to promote courses of lectures, summing up particular subjects so as to extend the general knowledge of Chemistry. This was very essential, as owing to the accumulation of detail, specialisation was very necessary, but the disadvantage of this was that persons were apt to have no great knowledge of, or interest in, the work of those engaged in other branches of their science. Chemistry was becoming more and more essential in all branches of life, and exercised a great influence in war and peace. That influence would increase, and he had no doubt that the Chemical Society would flourish in the future as it had done in the past.

Professor RAPHAEL MELDOLA, Past President of the Chemical Society, proposed the toast of "The City and Guilds of London," coupled with the names of Mr. F. A. Roberts, Master of the Worshipful Company of Grocers, and Mr. Walter S. Gardner, Master of the Worshipful Company of Drapers. It was a popular belief, declared Prof. Meldola, that City Companies were associated solely with City banquets and gorgeous palaces. As a servant of those Companies taking cognizance of what was going on in the upper regions, he could assure them that the holding of banquets was not their sole object of existence. We were perhaps familiar with their efforts in the cause of charity, but he wished to allude to the assistance they gave to the cause of education and science. It was thirty years since the cry of "Technical Education" was raised in this country. That cry meant that there was not a sufficiently close association between Science and Industry. The City and Guilds threw themselves into the breach, and boldly undertook the pioneering work of Technical Education in this country. They took over the work that the State had not touched hitherto, and the foundation of the City and Guilds of London Institute was the outcome; and during the period from 1878 to 1908, fifty-two City Companies contributed to that Institute £768,360 to advance the cause of British Technical Education.

Mr. F. A. ROBERTS, responding for the Worshipful Company of Grocers, reciprocated the kindly sentiments of Prof. Meldola. The Company were prepared to continue their good work, but hoped that there would be no outside interference with them, as he believed they were employing their money to the best interests of science, education, and charity.

Mr. WALTER S. GARDNER responded for the Worshipful Company

of Drapers, and referred to the useful work of their Company in the matter of apprentices, a work which they hoped would mitigate to some extent the evil of sending boys out at an early age to earn a few shillings a week for three or four years, after which they become practically unfit for anything of service to the community.

Professor H. A. Miers, proposing the toast of "Scientific Societies," coupled with the name of Sir Archibald Geikie, President of the Royal Society, said the tendency was for Societies to go on multiplying and specialising. The work of specialisation was becoming so serious that the fear was that when a paper was read at a Scientific Society nowadays, the only person who at all understood it was the author himself. Perhaps such a circumstance had its own field of usefulness, and he reminded them of the man who left £10,000 in his will to the Society whose meetings had proven such an excellent antidote to insomnia. He hoped that some method could be found to make use of the splendid amateur materials of which the various Scientific Societies consisted. Whether the Societies were making the best use of their opportunities or not, there was one extremely wholesome sign about their present state—they were in no danger of becoming a Joint Mutual Admiration Society, but were living in the bracing atmosphere of criticism which was undoubtedly useful in the promotion of their work as a whole.

Sir Archibald Geikie, in response, said that Science had grown enormously of late. There was the danger, as the President had pointed out, that specialisation would go on so far that the votary of one branch of science should be entirely unacquainted with what was taking place in another branch of it. It was a very bad thing, he declared, for a man to live in water-tight compartments of knowledge. It would enlarge his views if he took in something from other spheres of knowledge. Something, he was glad to say, was being done in that direction, and none of the Societies moving that way had attained greater success than the Chemical Society.

Professor J. Emerson Reynolds proposed the toast of "The Guests," and alluded in warm terms to Lord Balfour of Burleigh and Sir James Crichton-Browne, whose names were coupled with the toast.

Lord Balfour of Burleigh responded as the unworthy representative of the Church, which had disappeared, of the law which was still worthily represented, and of various educational authorities whom he saw before him, and to whom he had been in servitude on former occasions.

Sir James Crichton-Browne, also responding to the toast of "The Guests," said it was delightful to know that the members of the Royal Family, including His Majesty the King, were showing a great and intelligent interest in the work of the Royal Institution, which he, Sir James represented. That interest was being extended to the

forthcoming Congress at the Albert Hall. As to the general outlook, we had fallen upon lean years. We had with us Unemployment and sombre anticipations of the next Budget. We looked to the Chemists for new knowledge which should not only enable us to redress some of the evils we saw around us, and, in a utilitarian sense, largely add to the comfort and convenience of human life, but which, better still, should make for the clarification of our conceptions of the Universe and for the refinement and ennobling of our lives.

Thursday, April 1st, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, M.A., F.R.S., President, in the Chair.

It was announced that the Council had appointed the following Committees for 1909—1910:

Finance Committee: Messrs. E. G. Hooper, G. T. Moody, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee: Messrs. W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee: Messrs. E. C. C. Baly, F. D. Chattaway, B. Dyer, W. Gowland, A. Harden, C. A. Keane, A. Lapworth, E. J. Mills, J. M. Thomson (Chairman), J. A. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee: Messrs. W. R. Dunstan, C. E. Groves, J. T. Hewitt, A. McKenzie, R. Meldola, G. T. Morgan, T. E. Thorpe, and the Officers.

Research Fund Committee: Messrs. G. T. Beilby, J. N. Collie, A. D. Hall, A. Liversidge, R. Meldola, R. Messel, Sir A. Pedler, W. H. Perkin, J. E. Reynolds, W. A. Tilden, and the Officers.

Certificates were read for the first time in favour of Messrs.:

John Harold Edge, Great Marld, Smithills, Bolton.
Harold Hibbert, M.Sc., Ph.D., Creston, Marple Bridge, Derbyshire.
Roland Josiah May, Granaugh Villa, Dunbar, N.B.
Thomas Napier, Arbiene, Clarkston, Busby.

Of the following papers, those marked * were read:

***97. "The affinity values of certain alkaloids."**
By Victor Herbert Veley.

Determinations have been made of the affinity value of some of the more important alkaloids by the methyl-orange and borax precipitation methods, the latter only being put forward as giving approximate

results in cases in which the electric conductivity and ester catalysis methods cannot be applied.

It was shown that the affinity values of only a few alkaloids are less than $1 \cdot 10^{-7}$, those of the greater number are between the limits of $1 \cdot 10^{-7}$ and $3 \cdot 10^{-5}$ (value of ammonia), and lastly, only a few have a value higher than the last figure, and hence may be classed with the tetra-alkylammonium hydroxides.

It appears that when alkaloids consist of two conjoint residues which, if considered each by itself, would give affinity values of a widely different order, such as piperidine or benzylamine, on the one hand, and quinoline or pyrrolidine, on the other, the stronger residue is modified by the presence of the weaker. It seems to be immaterial whether each residue contains a nitrogen atom, and whether such an atom is common to both.

The affinity values determined by the methods applied, and collected together for the sake of comparison, illustrate the difficulty of obtaining salts, B,2HCl, in the case of certain dinitrogen alkaloids.

Discussion.

Prof. Kipping understood that the author's method was based on the first appearance of a permanent precipitate of the alkaloid; but as some alkaloids were soluble in solutions of some salts, a fact which was often observed in dealing with compounds containing silicon, he asked if the formation of a precipitate indicated corresponding conditions in all cases?

Dr. Lessing asked the author if he had found any marked difference in affinity values of tropine derivatives with the nitrogen in the α- and β-positions respectively to the carboxyl group. Willstätter and he found some years ago that with regard to exhaustive methylation, pyrrolidine- and piperidine-carboxylic acids may be classified into two groups, namely, those of the ecgonine type, corresponding with β-amino-acids, in which methylation effects the disruption of the ring, and those of the α-ecgonine type, corresponding with α-amino-acids, which resist all attempts to open up the ring.

Dr. Veley replied that the point of initial precipitation of the alkaloid by the hydrolysed borax solution was perfectly sharp in all cases examined with the single exception of papaverine; the precipitate initially formed redissolved at first quickly, and subsequently more slowly. The method proposed could only be applied for alkaloids the solubility of which in water was of the order 1 : 1000.

The affinity values of tropine and its derivatives had been dealt with in a previous communication.

There appeared to be a certain confusion in the minds of certain writers between basicity and affinity values; although there was, doubtless, some correlation between these two factors, yet in the present state of our knowledge it appeared prudent to keep them quite distinct from one another.

*98. "Phycoerythrin, the pigment of the red algæ." By Edward Kenneth Hanson.

Phycoerythrin has been investigated as to (1) its action with regard to light and (2) its chemical nature. With respect to the first point, Schütt (*Ber. Deut. bot. Ges.*, 1888, **6**, 307) has shown that phycoerythrin absorbs bluish-green light and gives an orange fluorescence. The author has confirmed this observation and has further photographed the fluorescence spectrum, thus succeeding in demonstrating that the fluorescent light gives *two* bands coincident with two of the absorption bands of chlorophyll. This is in harmony with the hypothesis that phycoerythrin assists assimilation in deep-water plants by absorbing the light available at these depths and degrading it to yellow and red light which can be utilised by the chlorophyll.

With regard to the chemical nature of phycoerythrin, the evidence is very inconclusive, owing to the impossibility (up to the present) of obtaining pure phycoerythrin. Molisch (*Bot. Zeit.*, 1894, 177) has suggested that the pigment is protein; but it does not give the biuret reaction, and its nitrogen-content is too low (not much greater than 6 per cent.) for a true protein. It is, however, a colloid, soluble only in water, and precipitated by the ordinary protein precipitants, and appears to be related to proteins, as it yields leucine on hydrolysis with acids. It is attacked by trypsin, but not by pepsin.

Discussion.

Mr. Chaston Chapman said it had occurred to him that the colouring matter of certain red torulæ which he was examining, and which appeared to be very closely allied to carotene, might conceivably be of some assistance to the organism in protecting the protoplasm from the injurious effects of the violet rays of light. He had made experiments on this point and had found that these organisms, unlike many of the yeasts, grew equally well whether exposed to red or violet rays. He did not see, however, that in the case of the algæ referred to by the author, any such protective effect could come into play.

Dr. Feilmann suggested that dyeing experiments on the material might throw some light on the chemical nature and composition

of the colouring principle; it might, for instance, be possible in this way to discover whether the substance contained nitrogen, by dyeing on to cotton and then testing for that element.

The PRESIDENT asked how the author was sure that algin was not precipitated with the colouring matter.

In reply, Mr. HANSON said that no experiments had been made in dyeing. The solution of phycoerythrin in pure water deteriorated very rapidly, but the presence of a small amount of eucalyptus oil or other antiseptic enabled solutions to be kept, even if exposed to light, for months. In answer to the President's questions, he did not consider that separation from algin was complete: that was, indeed, the chief difficulty in attempting to study the chemical nature of phycoerythrin. Boiling with sodium carbonate decolorised the solution. With regard to Dr. Cain's suggestion, the solid material had not been tested for bromine or iodine, and although it gave a qualitative reaction for sulphur, an amount sufficient for quantitative estimation had not been found.

***99. "*iso*Amygdalin and the resolution of its hepta-acetyl derivative." By Frank Tutin.**

Since *iso*amygdalin crystallises only with difficulty, and melts indefinitely at relatively so low a temperature (125—140°), the author considers that it does not consist of a definite, partially racemic compound, but is merely a mixture of amygdalin and the corresponding derivative of *d*-mandelonitrile. Moreover, it appears that the latter derivative predominates, since the mandelic acid yielded by *iso*amygdalin is slightly dextrorotatory.

As *iso*amygdalin itself cannot be fractionally crystallised in a satisfactory manner, its acetyl derivative has been employed. This has been separated into its components, namely, hepta-acetylamygdalin and the hepta-acetyl derivative of the unknown stereoisomeride of amygdalin. *Hepta-acetyl*neo*amygdalin*, $C_{34}H_{41}O_{18}N$, crystallises in long needles, melts at 174°, and has $[\alpha]_D - 65{\cdot}6°$ in chloroform. On hydrolysis with concentrated hydrochloric acid, it yields *d*-mandelic acid.

***100. "The stability of compounds derived from tertiary amines and magnesium alkyl halides." By Harold Hibbert.**

A determination of the chemical "*affinergy*" of diethylaniline for magnesium methyl iodide by the method previously described by the author (this vol., p. 57) shows a very low value relative to that of mono-

ethylaniline. This is in agreement with the observation of Tschelinzeff (*Ber.*, 1907, **40**, 1495), that the heat of combination of diethylaniline with magnesium propyl iodide is very small. It follows from these two facts that the quaternary compound, $NEt_2Ph \cdot MgMeI$, must be relatively very unstable. The author has been able to show that this instability is a general property of the compounds derived from tertiary amines, decomposition into free base and magnesium alkyl halide occurring at 200—280°. This is true of the derivatives from triethylamine, tripropylamine, diethylaniline, and dimethylaniline; pyridine forms an exception. The original amine is obtained whether magnesium ethyl bromide or magnesium methyl iodide is employed, and this point is being investigated with a larger number of alkyl halides.

***101. "A new method for the separation of tertiary from secondary and primary amines." By Harold Hibbert and Archibald Wise.**

The relative instability of the derivatives from tertiary amines and magnesium alkyl halides (see preceding note) led the authors to investigate the stability of the compounds derived from the action of magnesium alkyl halides on secondary and primary amines. It has been found that the derivatives R_2NMgI and $RNHMgI$ respectively are very stable substances, only decomposing when strongly heated, whereas the derivatives with tertiary amines decompose between 200° and 280°. Based on these facts the following simple method has been devised for the separation of tertiary amines from mixtures with secondary and primary amines: to the mixture of amines (either alone or in ethereal solution) is added a quantity of an ethereal solution of magnesium ethyl bromide sufficient to combine with the whole of the secondary (or primary, respectively) amine, together with 20—30 per cent.* of the theoretical amount required for the tertiary amine, and the product then distilled from an oil-bath. Ether distils over at first, followed as the temperature in the oil-bath rises to 200—280° by the pure tertiary amine. The last traces are swept out by dry hydrogen or other indifferent gas. The secondary (or primary, respectively) amine is recovered by adding water and distilling in a current of steam. Even when using very small quantities (for example, 5—10 grams) it is possible to recover 70—80 per cent. of the products in this way, and the tertiary amine is obtained quite free from secondary or primary amine. The method has been applied to the separation of the following mixtures: di- and tri-ethylamine, di- and

* This amount is sufficient on account of the very great difference in their chemical "*affinergies*" for the Grignard reagent.

tri-propylamine, mono- and di-methylaniline, mono- and di-ethylaniline, aniline and dimethylaniline.

102. "The preparation and properties of the *N*-tribromo-substituted hydrazines (the diazonium perbromides)." By Frederick Daniel Chattaway.

The preparation of the *N*-tribromophenylhydrazines from the hydrazines by substitution was described.

All the *N*-tribromohydrazines when brought into contact with free bromine combine with it and form compounds only stable under a considerable pressure of bromine vapour, in which the halogen is much less firmly attached than when replacing hydrogen combined with tervalent nitrogen.

In the preparation of the *N*-tribromohydrazines from diazonium salts, if liquid bromine is used, these unstable compounds are formed locally and have to be removed from the solid substituted hydrazines by washing with ether or exposure to the air. They are also formed when the *N*-tribromohydrazines are placed in water, these compounds being in part dissociated into diazonium salts and free bromine, the halogen set free combining to a considerable extent with the remainder of the *N*-substituted hydrazines and forming with them a more or less pasty mass.

The behaviour of a number of *N*-tribromohydrazines when heated, when exposed to dry and moist air, when suspended in water or concentrated hydrochloric acid, and when dissolved in alcohol or acetic acid was also described.

103. "The coloured salts and derivatives of the thiovioluric acid group." (Preliminary note.) By Percy Claude Cameron Isherwood.

In view of the interesting colour relations of the salts of the violuric acid group, the author is studying the influence of the replacement of oxygen by sulphur in this acid and some of its derivatives.

Thiovioluric Acid, $CS\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C{:}N\cdot OH$.—The *monosodium* salt of this acid has been prepared by the action of acetic acid on equivalent quantities of sodium thiobarbiturate and sodium nitrite in aqueous solution below 0°. From this the free acid was obtained in small, yellow needles by the action of cold dilute hydrochloric acid. Its aqueous solution has the characteristic violet colour. The following salts have been prepared and exhibit a wide range of colours: *lithium*,

sodium, potassium, ammonium, calcium, strontium, barium, magnesium, mercuric, lead, silver, and *cadmium.*

1 : 3-*Diphenylthiobarbituric Acid,* $CS<^{NPh\cdot CO}_{NPh\cdot CO}>CH_2$.—This was prepared by heating together *s*-diphenylthiocarbamide, phosphoryl chloride, and malonic acid (compare Miss Whiteley, *Trans.*, 1907, **91**, 1330); it crystallises from alcohol in bulky, pale yellow needles.

1 : 3-*Diphenylthiovioluric Acid,* $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}N\cdot OH$.—1 : 3-Diphenylthiobarbituric acid was dissolved in dilute ammonia and treated successively with equivalent quantities of sodium nitrite and acetic acid. A reddish precipitate of the above acid was formed. The work is being extended to other derivatives of thiovioluric acid, especially with a view to the examination of the colour and absorption spectra of solutions of salts.

104. "Studies in the barbituric acid series. Part II. 1 : 3-Diphenyl-2-thiobarbituric acid and some coloured derivatives." By Martha Annie Whiteley and [the late] Harold Mountain.

In a recent paper by Hantzsch, "*Über Pantochromie und Chromoisomerie von Violuraten und verwandten Oximidoketon-Salzen*" (*Ber.*, 1909, **42**, 966), two references are made to work that is being conducted by R. Robison on diphenylvioluric acid; as this compound, the first of the aryl-substituted violuric acids, and a large number of its salts and derivatives were prepared by one of the authors (Whiteley, *Trans.*, 1907, **91**, 1330), and the work is still being continued, it was deemed advisable to describe further results obtained in this series.

1 : 3-*Diphenyl-2-thiobarbituric acid,* $CS<^{NPh\cdot CO}_{NPh\cdot CO}>CH_2$, m. p. 244°, forms pale yellow needles, and condenses with aldehydes and ketones to yield compounds of the type $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}R$, which are reduced to the corresponding saturated derivative, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>CH\cdot HR$; 5-iso*propenyl*-1 : 3-*diphenyl-2-thiobarbituric acid,*

$$CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}CMe_2,$$

m. p. 260—262°, forms canary-yellow prisms; 5-iso*propyl*-1 : 3-*diphenyl-2-thiobarbituric acid,* m. p. 237—240°, is pale yellow; 5-*benzylidene*-1 : 3-*diphenyl-2-thiobarbituric acid,* $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}CHPh$, m. p. 254°,

forms orange-yellow prisms; *5-benzyl-1 : 3-diphenyl-2-thiobarbituric acid*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>CH\cdot CH_2Ph$, m. p. 187°, forms pale yellow needles; *5-o-nitrobenzylidene-1 : 3-diphenyl-2-thiobarbituric acid*,

$$CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}CH\cdot C_6H_4\cdot NO_2,$$

m. p. 236°, forms dull orange needles, and *5-cinnamylidene-1 : 3-diphenyl-2-thiobarbituric acid*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}CH\cdot CH{:}CHPh$, m. p. 278°, forms brilliant, crimson, prismatic needles.

1 : 3-Diphenyl-2-thiobarbituric acid and its 5-aryl-substituted derivatives condense with aromatic diazonium chlorides to form the corresponding hydrazone or azo-derivative: *1 : 3-diphenyl-2-thioalloxan-phenylhydrazone*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}N\cdot NHPh$, m. p. 291°, forms brilliant, orange, prismatic needles; *1 : 3-diphenyl-2-thioalloxan-p-nitrophenylhydrazone*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}N\cdot NH\cdot C_6H_4\cdot NO_2$, m. p. 288°, crystallises in orange-red needles, and *5-benzeneazo-1 : 3-diphenyl-5-benzyl-2-thiobarbituric acid*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{CH_2Ph}_{N:NPh}$, m. p. 135°, crystallises in yellow needles.

Two isomeric varieties of 1 : 3-diphenyl-2-thiovioluric acid have been obtained differing in colour and melting point, and a similar isomerism has been observed among the pyridine, piperidine, and alkali salts of the acid. *α-1 : 3-Diphenyl-2-thiovioluric acid*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}N\cdot OH$, m. p. 211—212°, obtained by the action of ethyl nitrite on 1 : 3-diphenyl-2-thiobarbituric acid, forms deep red, prismatic needles, and a bluish-violet hydrated *acid*, $CS<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}N\cdot OH,H_2O$, is obtained by the action of sodium nitrite and hydrochloric acid on the barbituric acid; *β-1 : 3-diphenyl-2-thiovioluric acid* (probably),

$$CS<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{NH}_{O},$$

m. p. 224°, is obtained as a yellowish-brown, crystalline powder when the pyridine salt is heated at 100° or boiled with alcohol. The *piperidine* salt, $C_{16}H_{11}O_3N_3S,C_5NH_{11}$, exists in two crystalline forms, one grey, m. p. 181—182°, and one pale red, m. p. 187°; the two varieties of the *pyridine* salt, $C_{16}H_{11}O_3N_3S,CNH_5$, are green and dull red respectively. The *potassium* salt, $C_{16}H_{10}O_3N_3SK$, is obtained in dark olive-green, cubic crystals by the action of potassium hydroxide on the α-violuric acid; the *sodium* salt, $C_{16}H_{10}O_3N_3SNa$, is similarly obtained in rose-red needles; when, however, an alcoholic solution of 1 : 3-diphenyl-2-thiobarbituric acid is added to an aqueous

solution of potassium or sodium nitrite, the potassium or sodium salt of 1 : 3-diphenyl-2-thiovioluric acid is obtained as a violet or purple, microcrystalline powder respectively. The *ferrous* salt, $(C_{16}H_{10}O_3N_3S)_2Fe$, is a deep blue, crystalline powder with a purple reflex.

The melting points recorded in this preliminary communication are in all cases temperatures of decomposition, and therefore vary with rate of heating.

105. "Nitrosoacetylamino-derivatives of the benzene and diphenyl eries." By John Cannell Cain.

In continuation of previous work (*Trans.*, 1908, **93**, 681), the author has prepared the following compounds: 2-*Nitrosoaceto*-p-*toluidide*,

$$NO\cdot C_6H_3Me\cdot NHAc,$$

pale yellowish-brown crystals, m. p. 195°; 6-*nitroso*-m-*toluidide*, green needles, m. p. 128—129°; 5-*nitrosoacsto*-o-*toluidide*, green needles, m. p. 135—136°; 2-*chloro*-4-*aminoacetanilide*, $NH_2\cdot C_6H_3Cl\cdot NHAc$, pale yellow plates, m. p. 111°; 2-*chloro*-4-*nitrosoacetanilide*, green needles, m. p. 112—113°, and 3 : 3′-*dichloro*-4 : 4′-*diacetyldiaminoazobenzene*,

$$NHAc\cdot C_6H_3Cl\cdot N_2\cdot C_6H_3Cl\cdot NHAc,$$

pale yellow needles, m. p. 280°.

The monoacetyldiamines of the diphenyl series can readily be prepared by the action of acetic anhydride on an aqueous alcoholic solution of the corresponding base. *Monoacetyltolidine*,

$$NHAc\cdot C_6H_3Me\cdot C_6H_3Me\cdot NH_2,H_2O,$$

forms white, shining plates, m. p. 103°, and on oxidation with Caro's acid yields 4-*nitroso*-4′-*acetylamino*-3 : 3′-*ditolyl*,

$$NO\cdot C_6H_3Me\cdot C_6H_3Me\cdot NHAc,$$

pale brown crusts, m. p. 154—155°. Monoacetylbenzidine on similar treatment furnishes 4-*nitroso*-4′-*acetylaminodiphenyl*,

$$NO\cdot C_6H_4\cdot C_6H_4\cdot NHAc,$$

yellowish-brown, feathery needles, m. p. about 275°.

106. "The rate of reaction of the triphenylmethane dyes with acid and alkali. Part. II. Brilliant green and malachite green." By Nevil Vincent Sidgwick and Tom Sidney Moore.

In a previous paper (*Zeitsch. physikal. Chem.*, 1907, **57**, 385) the authors have investigated the rate of reaction of brilliant green (the salt of tetraethyldiaminotriphenylcarbinol) with alkali and with hydrochloric acid. They have now examined the action of nitric acid on this dye, and that of nitric and hydrochloric acids and of alkali on

the corresponding tetramethyl compound, malachite green. The method adopted in all cases was to determine the concentration of the dye by measuring the colour of the solution in a Donnan tintometer.

The behaviour of the two dyes was found to be very similar, and also that of the two acids.

(1) The velocity of formation of the carbinol in presence of alkali is proportional to the product of the concentrations of the dye and the alkali, and is found to be more than twice as great as that deduced for much higher concentrations by Gerlinger (*Ber.*, 1904, **37**, 3958) from the conductivity measurements of Hantzsch and Osswald (*Ber.*, 1900, **33**, 278). This is probably due to the dye-base not being wholly ionised, and would be accounted for by a dissociation constant of 0·00531, about four times that of diethylamine.

(2) Acids act on the dye-salt to form a colourless acid salt, and at equilibrium $k_1 \times C_{\text{dye-salt}} \times C_{\text{acid}} = k_2 \times C_{\text{acid salt}}$, where k_1/k_2 is independent of the strength of the acid, but k_1 and k_2 vary inversely as the cube root of the concentration of the acid.

(3) When a solution of the carbinol is treated with acid, it first yields the dye-salt, which is then converted reversibly into the acid salt. The velocity of this last reaction being known, that of the first can be determined. A graphic method, due to Mr. H. G. J. Moseley, was described, by which the velocity can be calculated from the somewhat complicated expression obtained, which does not admit of direct solution. The velocity is proportional to the concentration of the carbinol, and to the two-thirds power of that of the acid.

The various constants obtained for the two dyes and for the two acids show a very close agreement, the difference never amounting to 25 per cent., and in most cases being much smaller.

107. "The rate of reaction of the triphenylmethane dyes with acid and alkali. Part III. Diaminotriphenylcarbinol." By Nevil Vincent Sidgwick and Albert Cherbury David Rivett.

The velocity of reaction of this unsubstituted dye was determined by the same method. The general results are similar, but the constants are all larger, and certain modifications are introduced by the fact that this dye is a much weaker base.

(1) With alkali the reaction is unimolecular as before, but the constant increases much more slowly than the alkali, owing no doubt to the dye-base being largely undissociated. The observed results agree with those calculated for a dissociation constant of 0·0004 (about 1/12 of that of brilliant green) when the alkali is not too weak. They indicate that if the carbinol is formed from the non-ionised portion of the dye-base, this dye reacts 1·6 times as fast as brilliant green,

but if from the ions, 21 times as fast. The former view is therefore more probable.

(2) If a solution of the dye is treated with a small quantity of acid, its colour increases, owing to the disappearance of hydrolysis, whilst a further addition of acid diminishes the colour, from the formation of the acid salt. In *N*/125,000-solution the dye is hydrolysed to the extent of 33·5 per cent., giving the dissociation constant of the base as $7{\cdot}5 \times 10^{-9}$. This obviously refers to the system (carbinol $\rightleftharpoons$ dye-base) at equilibrium, and is 50,000 times less than the constant of the dye-base itself. This is an instance of the true "abnormal hydrolysis" of a pseudo-base.

The constants k_1 and k_2 of the formation and dissociation of the acid salt (see preceding paper) vary inversely as the square root (instead of the cube root) of the concentration of the acid.

(3) The action of acid on the carbinol is the same as in the previous cases, the unimolecular constant M being proportional to the two-thirds power of the strength of the acid.

The values of these constants (compared by reference to a normal acid) are in all cases higher for this dye than for the alkylated derivatives, brilliant green and malachite green, k_1 being about 7 times, k_2 1·5 times, and M 3 times as great.

108. "Indican. Part II." By Arthur George Perkin and Frederick Thomas.

p-Nitrobenzaldehydeindogenide, $C_{15}H_{10}O_3N_2$ (Baeyer, *Ber.*, 1881, **14**, 1745), is readily formed by hydrolysing indican with acid in the presence of *p*-nitrobenzaldehyde, and the reaction may be employed for the quantitative estimation of the glucoside. In this respect piperonal is not so serviceable, and the yield of *methylenedioxybenzaldehydeindogenide* $C_{16}H_{11}O_3N$, orange needles, m. p. 223—224°, by the process employed was but 96 per cent. *Dihydroxybenzaldehydeindogenide*, $C_{15}H_{11}O_3N$, from indican, acid, and protocatechualdehyde, orange-red needles, m. p. 264—265°, soluble in strong alkali with a blue colour, and dyeing mordanted fabrics, is more difficult to isolate, owing to the formation of brown secondary products. The *acetyl* derivative,

$$C_{15}H_9O_3N(C_2H_3O)_2,$$

orange needles, melts at 182°. *Hydroxybenzaldehydeindogenide*, from *p*-hydroxybenzaldehyde, $C_{15}H_{11}O_2N$, orange-red needles, m. p. 267—269°, soluble in alkali with a red coloration, gives the *acetyl* compound, $C_{15}H_{10}O_2N,C_2H_3O$, orange leaflets, m. p. 223—224°, and is not a dyestuff. The *p*-nitro- and methylenedioxy-benzaldehydeindogenides can easily be prepared in quantity by employing the leaf extracts of *I. sumatrana* and *I. arrecta* in the place of pure indican.

When indican is hydrolysed by sulphuric acid (4 c.c in 1000 c.c. of water) at 60°, simultaneously oxidising with air, the yield of colouring matter is but 85 per cent., due in part to the formation of brown secondary products. The latter reaction does not so readily occur when the equivalent quantity of hydrochloric acid is employed, and the yield of colouring matter (about 93·5 per cent.) is thus higher. In addition to indigotin, indirubin is also formed in some quantity under these conditions. Stronger solutions of sulphuric and hydrochloric acids at the boiling point in absence of air give respectively with indican identical brown products insoluble in alkali, from which, in addition to the indoxyl brown previously described (*Trans.*, 1907, **91**, 1715), an analogous substance more sparingly soluble in alcohol (Found, N = 9·65) was isolated.

The action of acid in the cold for a longer period (compare Schunck and Roemer, *Ber.*, 1879, **12**, 2311) has a similar effect, and indoxyl brown is thus formed. The brown product obtained from the leaf extracts of the *Indigoferae* by means of acid differs from indoxyl brown in that it is soluble in alkali, and appears to arise from a condensation of indoxyl with other compounds derived from the plant. In view of recent discussion on the melting point of dextrososazone (Tutin, *Proc.*, 1907, **23**, 250), the pure sugar derived from indican was converted into its acetyl derivative, and this was identical with acetyldextrose.

109. "Indican. Part III." By Frederick Thomas, William Popplewell Bloxam, and Arthur George Perkin.

The authors have carried out experiments on the hydrolysis of pure indican by means of indimulsine, its specific enzyme (Beyerinck, *Proc. K. Akad. Wetensch. Amsterdam*, 1899, **1**, 120; Hazewinkel, *ibid.*, 1900, **2**, 512, and van Romburgh, *ibid.*, 1899, **2**, 344), and on the air oxidation of the solutions of indoxyl thus produced under a variety of conditions. The results indicate that, owing to the unstable nature of indoxyl, changes occur both during the fermentation and oxidation processes which prevent these reactions from proceeding in a quantitative manner. The best yields of colouring matter were given when a small amount of acid was present during the fermentation (compare Beyerinck, *loc. cit.*), and the fermented liquid was then oxidised in the presence of a trace of ammonia.

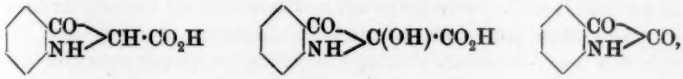
110. "Indoxylic acid." By Arthur George Perkin.

The examination of a sample originally consisting of commercial indoxylic acid, which had remained unopened for some years, showed

that no indoxyl or indoxylic acid was now present. The product contained:

Matter soluble in alkali	32·94 per cent.
Indirubin	42·37 ,,
Indigotin	17·30 ,,
Moisture	2·15 ,,
Ash	1·05 ,,
Insoluble in nitrobenzene by difference	4·19 ,,

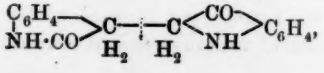
The oxidation involved appears to have arisen from the gradual admission of air, and whereas the formation of indigotin is easily accounted for, it is considered that the predominance of indirubin has arisen from the formation, in the first place, of isatin from ψ-indoxylic acid, thus:



and its subsequent condensation with indoxyl. That portion of the matter soluble in alkali contained isatin and an acid resembling phenylglycine-*o*-carboxylic acid, but the main bulk consisted of an amorphous, brown product, from which was isolated a brown substance very closely resembling and possibly identical with the chief constituent of the indigo-brown (*Trans.*, 1907, **91**, 279) which is present in natural indigo. The examination of two other products derived in the same manner from indoxylic acid gave results of a similar character, and it thus appears likely that in these circumstances the changes involved are of a normal character.

111. "The reduction of indirubin." By Arthur George Perkin.

It has been shown by Fasal (*Mitt. K. Tech. Gew-mus. Wien*, 1895, 307) that when indirubin is reduced by zinc dust and alkali under conditions of indigo-vat practice, the indirubin-white at first formed soon undergoes further reduction, indoxyl being thus produced, and this in the dyeing operation is converted into indigotin. A study of the reaction with a large quantity of indirubin derived from an extract of *I. sumatrana* by means of isatin has shown that under these conditions oxindole is also produced, and this, obtained in colourless needles, m. p. 120°, was identified by means of its nitroso-compound, m. p. 204—206°, and by oxidation with ferric chloride to isatin. The formation of indoxyl and oxindole is readily understood by reference to the following scheme:



and the behaviour of indirubin in this respect does not suggest that its presence in natural indigo can be economically advantageous. In addition to oxindole, a small quantity of a yellow basic substance resembling the di-indole of Schutzenberger (*Jahresb.*, 1877, 511), $C_{16}H_{14}N_2$, was also formed in this reaction. A quantitative study of the reduction of indirubin by this method is in progress.

112. "Solubility of lead sulphate in concentrated solutions of sodium and potassium acetate." By John Jacob Fox.

The increased solubility of lead sulphate in concentrated solutions of sodium and potassium acetates is due to the formation of lead acetate in solution, conclusive evidence being obtained from the examination of the system potassium acetate–lead sulphate. In this case no sulphate was dissolved, although as much as 19 per cent. of lead acetate was found in one of the solutions. As regards the system sodium acetate–lead sulphate, the proportion of sulphate in solution was equivalent to the lead dissolved.

The solid phase in the potassium acetate system was altered, lead potassium sulphate, $PbK_2(SO_4)_2$, being formed, but no corresponding double salt was obtained from the sodium acetate system. The absence of double salt in the latter case probably arises from the fact that the amount of sodium sulphate formed from the lead sulphate by sodium acetate is insufficient, considered alone, to saturate the solution at 25°. The solubility curve for sodium sulphate in sodium acetate solution is entirely different in character from that of potassium sulphate in potassium acetate, the solubility in the latter case decreasing rapidly with increasing concentration of the potassium acetate.

Although the solubility of lead sulphate is shown to be due to the formation of lead acetate in solution, the solubility curves do not coincide with those derived from the system lead acetate–alkali acetate, since the presence of sulphates in the solid phases tends to reduce the solubility o the lead.

113. "The colour and constitution of the alkyl iodides of cyclic bases." By Charles Kenneth Tinkler.

From an examination of the absorption spectra of the methiodides of cyclic bases, it is suggested that the colour of the alkyl iodides is due to polymerisation, the linking taking place between the iodine atoms.

A similar view was recently put forward by Hantzsch (*Ber.*, 1909, 42, 68). The results of molecular-weight determinations in support

of this view were communicated to Dr. Decker by the author in November, 1907, but were not published.

Phenylacridine methiodide in chloroform is termolecular, and the solution, like the solid substance, is strongly coloured (compare Hantzsch, *loc. cit.*).

Molecular-weight determinations carried out in diphenylamine solution by the cryoscopic method also indicate that the substances when coloured are polymerised. It was pointed out that the alkyl iodides of piperidine and tetrahydroquinoline derivatives are colourless.

114. **"A method for investigating dissociation equilibria in solutions, and its application to the study of aqueous potassium mercuri-iodide solutions." By Harry Medforth Dawson.**

A method for the investigation of dissociation equilibria in solutions was described. The type of equilibrium in question may be represented by the reversible equation $A + mB \rightleftharpoons AB_m$, according to which one mol. of the substance unites with m mols. of B to form the dissociating complex compound AB_m.

The method consists in adding to the solution of A and B a third substance C, which also combines with A to form a dissociating compound AC_n, the dissociation constant of which is known. If the concentration of uncombined C in the solution is determined, that of the compound AC_n follows at once, and by combining these data with the dissociation constant of the compound AC_n, the concentration of uncombined A in the solution can be obtained. Under certain conditions this leads at once to a knowledge of the molar ratio of A to B in the compound AB_m.

The method has been applied to the examination of solutions of mercuric iodide in potassium iodide. The experimental results show that the amount of potassium iodide which is combined with a given quantity of mercuric iodide diminishes as the relative concentration of the mercuric iodide in the solution increases. In solutions which contain relatively little mercuric iodide, the compound $2KI,HgI_2$ is the chief complex constituent; on the other hand, solutions which are nearly saturated with mercuric iodide contain the complex compound $3KI,2HgI_2$ as the chief constituent.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Geological Society of London. The Centenary. Celebrated September 26th to October 3rd, 1907. Recorded by *W. W.* **Watts.** pp. iv + 166. ill. London 1909. (*Recd.* 6/3/09.) From the Society.

Simmons, *William Herbert,* and **Appleton,** *H. A.* The handbook of soap manufacture. pp. vii + 159. ill. London 1908. (*Recd.* 18/3/09). From Mr. W. H. Simmons.

II. *By Purchase.*

Henrich, *Ferdinand.* Neuere theoretische Anschauungen auf dem Gebiete der organischen Chemie. pp. xiv + 294. Braunschweig 1908. (*Recd.* 25/3/09.)

Meyer, *Hans.* Analyse und Konstitutionsermittelung organischer Verbindungen. 2nd edition. pp. xxxii + 1003. Berlin 1909. (*Recd.* 31/3/09.)

Möhlau, *Richard,* and **Bucherer,** *Hans Th.* Farbenchemisches Praktikum zugleich Einführung in die Farbenchemie und Färbereitechnik. pp. x + 374. ill. Leipzig 1908. (*Recd.* 31/3/09.)

Parry, *Ernest J.* The chemistry of essential oils and artificial perfumes. 2nd edition. pp. viii + 546. ill. London 1908. (*Recd.* 25/3/09.)

Volhard, *Jacob.* Justus von Liebig. 2 vols. pp. xii + 456, viii + 438. ill. Leipzig 1909. (*Recd.* 31/3/09.)

Wedekind, *E.* Die Entwicklung der Stereochemie des fünfwertigen Stickstoffs im letzten Jahrzehnt. (Sammlung, Vol. XIV). Stuttgart 1909.

III. *Pamphlets.*

Bihar Planters' Association. Report of the Indigo Research Station, Sirsiah, for the year 1908–1909. By *Cyril* **Bergtheil.** pp. 24. Calcutta 1909.

Blount, *Bertram.* The composition of commercial petrols. [Paper read before the Incorporated Institution of Automobile Engineers on March 10th, 1909.] pp. 6. London 1909.

Duvivier, *Carl.* Recherches sur la préparation électrolytique des composés du plomb. pp. 19. Malines 1909.

Golding, *John.* Adaptation. (From the *Report and Trans. Nottingham Nat. Soc.,* **56,** 1907–1908.)

WOLCOTT GIBBS MEMORIAL LECTURE.

The above lecture will be delivered by Professor Frank Wigglesworth Clarke at the Ordinary Scientific Meeting on **Thursday**, June 3rd, at **8.30** p.m.

At the next Ordinary Meeting, on **Thursday**, May **6th**, 1909, at **8.30** p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated :

"Affinity constants of hydroxy- and alkyloxy-acids." By A. Findlay, W. E. S. Turner, and Miss G. E. Owen.

"The absorption spectra of the nitrates in relation to the ionic theory." By E. C. C. Baly, Miss K. A. Burke, and Miss E. G. Marsden.

"The chlorination of acetanilide." By W. J. Jones and K. J. P. Orton.

"Esterification constants of substituted acrylic acids. Part IV." By J. J. Sudborough and M. J. P. Davies.

"Action of the halogens on aromatic hydrazines." By F. D. Chattaway.

"Studies in the camphane series. Part XXVI. Aryl derivatives of iminocamphor." By M. O. Forster and T. Thornley.

ERRATA.

1909. Pp. 65 and 81 *for* "Vol. 26" *read* "Vol. 25."

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, May 6th, 1909.

Bennett, Hugh Garner, M.Sc. (Leeds),
13, Spring Grove Terrace, Leeds.

Assistant Lecturer and Demonstrator at the Leather Industries Department of the University of Leeds. The candidate was a student at the Leeds University, 1902—1905, took then the degree of B.Sc. with First Class Honours in Chemistry, and has since been on the staff in the Leather Department. He was admitted to the degree of M.Sc. in 1907. He has published the following papers: "Studies in Chlorination. The Chlorination of the Isomeric Chloronitrotoluenes" (Cohen and Bennett, *J.C.S.*, 1905, 320); "A Method for the Examination of Marine Oils" (Procter and Bennett, *J. Soc. Chem. Ind.*, 1906, 798). A series of papers on the "Analysis of Tanning Materials" (*J. Soc. Chem. Ind.*, 1906, 251; 1906, 1203; 1907, 79; 1907, 455; 1907, 1186; *Collegium*, 1907, 37; 1908, 98.) "The Tannage of Sole Leather with Mimosa Bark" (*J. Soc. Chem. Ind.*, 1908, 1193).

Henry R. Procter. J. B. Cohen.
A. G. Green. Arthur Smithells.
William A. Bone.

Blackburn, Albert Riley,
"Marshville," Derby Road, Widnes, Lancs.

Senior Chemistry Master, Secondary Day and Municipal Technical School, Widnes. B.Sc. (London University). A.R.C.S. Fifteen years' experience as a teacher of Chemistry.

George Tate. Frank Baker.
Thomas J. Roberts. A. J. Allmand.
Henry Bassett, jun.

Burt, Frank Playfair,

Elmhyrst, Weston-super-Mare.

Student. B.Sc. (London). 1851 Exhibition Science Research Scholar, 1906–8. Researches on: (1) "Atomic Weight of Nitrogen, based on Analysis of Nitrogen Sulphide" (not yet completed); (2) "On the Atomic Weight of Chlorine," with Dr. R. W. Gray (abstract published in *J.C.S.*).

William Ramsay. A. W. Stewart.
N. T. M. Wilsmore. R. W. Gray.
Edward C. Cyril Baly.

Campbell, Walter,

Albert House, Westcliff-on-Sea, Essex.

Brewer and Brewer's Analyst. Eighteen months assistant to Mr. John Heron, and now acting as chemist to Messrs. Friary, Holyroyd, and Healey's Breweries, Ltd., Guildford, Surrey.

John Heron. F. Stanley Benton.
Arthur R. Ling. John M. Heron.
Alfred Chaston Chapman. *L. T. Thorne.*
Lawrence Briant.

Caulkin, Howard Alfred,

"Oaklands," Solihull, Warwickshire.

Analytical Chemist. Six years as pupil and assistant with Messrs. Southall Bros. and Barclay, Manufacturing and Analytical Chemists, Birmingham. B.Sc. (Lond.). A.I.C. (Analysis of Food and Drugs, etc.). Now Assistant Chemist to Midland Railway Co., Derby.

Percy F. Frankland. Thos. J. Murray.
Hamilton McCombie. C. K. Tinkler.
Alex. Findlay. E. W. Mann.

Chew, John Henry,

46, Lytham Road, Blackpool.

Chemist to the Blackpool Corporation Gas Department. Appointed Chemist to the Gas Department in 1905. Had charge of all Analytical work in connection with the above Gas department for the last four years, and assisting in same for the previous three years.

Douglas T. Setterington. C. J. Whittaker.
Thos. Duxbury. *Francis J. H. Coutts.*
George Naylor. *Chas. Horne Warner.*

Clarke, George,

Cawnpore.

Agricultural Chemist, Land Records and Agriculture Department, United Provinces, India. Chemistry Student, University College, Nottingham (1896—1901). Chemistry Demonstrator under Prof. Pope, F.R.S., Manchester Technical School. Fellow of the Institute of Chemistry. Formerly Teacher of Agricultural Chemistry [under Essex County Council]. Joint author (with F. S. Kipping) of a paper on "α-Amino-β-methylhydrindene," *Trans.*, 1903, 913, and (with Prof. W. J. Pope) on "The Resolution of Externally Compensated Dihydro-α-methylindole," *Trans.*, 1904, 1330. Author of a note on "A glucoside from Tephrosia purpurea," *Proc. Chem. Soc.*, 1909.

F. Stanley Kipping. W. J. Pope.
R. M. Caven. John Golding.
Henry J. S. Sand.

Cooke, Reginald Cyril Herbert,

17, St. Edmund's Terrace, Regent's Park, N.W.

Late Reduction Mine Manager. Educated at U.C.S., London, 5 years. Studied Chemistry for 2 years under Professor Meldola, Finsbury Technical College. Assistant Chemist, 3 years, to Mexican Gold and Silver Recovery Co. Reduction Mine Manager 3½ years to Consolidated Gold Fields of S. Africa, Rhodesia. Contributed a paper on "Treatment of Giant Mine Ore," Rhodesia, read before the C. M. M. Society of S. Africa, 21 Nov., 1908.

R. Meldola. E. W. Bealey.
John Castell-Evans. F. Henry Streatfeild.
George Dean.

Cooper, George Stanley,

Heaton House, Cleckheaton, Yorks.

Student of Chemistry. Intending to be Science Master. Studied for three years at King's College, London, and intend sitting for the B.Sc. exam. (Honours Chemistry) in October next. I desire to keep myself up to date in Chemistry and to keep in touch with research work in general.

John M. Thomson. Herbert Jackson.
Patrick H. Kirkaldy. *W. D. Halliburton.*
W. B. Bottomley.

Couch, Daniel Little,

9, Charlmont Road, Tooting, S.W.

Analytical and Technical Chemist. Student at Battersea Polytechnic and Central Technical College. Assistant Chemist at Messrs.

Brooke, Simpson and Spiller, Ltd., Hackney. Chemist at Walter Voss & Co., Ltd., Millwall, E.

S. G. Rawson. J. L. White.
J. Wilson. J. Hart Smith.
J. C. Cain.

Couzens, Edward Gordon,
47, Allfarthing Lane, Wandsworth.

Assistant Demonstrator, Royal College of Science. First Class Associateship of Royal College of Science in Chemistry. Second Class Honours B.Sc., London.

William A. Tilden. G. T. Morgan.
M. O. Forster. James C. Philip.
W. O. Wootton.

Creighton, Henry Jermain Maude,
Halifax, Nova Scotia, Canada.

Research Student. B.A. with High Honours and University Medal in Chemistry, Dalhousie University, 1906. M.A., Dalhousie University, 1907. 1851 Exhibition Science Research Scholar. Published: "Action of Radium on the Decomposition of Hydriodic Acid"; "A Few Chemical Changes Influenced by Radium, etc., etc."

Percy F. Frankland. Hamilton McCombie.
Alex. Findlay. Thomas H. Pope.
Adrian J. Brown.

Crewe, Philip Henry,
"Glencairn," Woods Moor, Stockport.

Analytical Chemist. Nine years Senior Assistant with Messrs. Jas. Woolley, Sons & Co., Ltd., Manufacturing Pharmaceutical Chemists, Manchester. *Author of*: Determination of Ferrous Carbonate in Pharmaceutical Preparations; Assay and Examination of Mercurial Ointment: read before the British Pharmaceutical Conference, 1907 and 1908.

L. G. Radcliffe. S. J. Peachey.
F. S. Sinnatt. John Allen.
Jul. Hübner.

Dyche-Teague, Francis Clifford,
8, Mount Road, Hendon, N.W.

Analytical Chemist and Bacteriologist. B.Sc., Birmingham; First Class in Chemistry. Late Assistant in Public Health Laboratory of

the Metropolitan Boro' of Stepney. Analyst and Bacteriologist to Messrs. B. Davies & Sons, King St., W., and private practice.

Albert E. Parkes.	Hamilton McCombie.
Percy F. Frankland.	Thos. J. Murray.
Alex. Findlay.	Fredk. T. Harry.

Fowler, William,

3, Cranbrook Road, Victoria Docks, E.

Sugar Chemist. Eight years' connexion with Sugar Refining, and during the last year considerable experience with Brewing Sugars and Syrups, etc. Student at East Ham Technical College from 1905 until 1907. Student at Finsbury Technical College since 1907.

L. J. de Whalley.	Chas. R. Darling.
Arthur R. Ling.	J. Castell-Evans.

E. W. Bealey.

Grist, Charles James,

Apsley House, Banstead, Surrey.

Metallurgist. Taught Inorganic Chemistry in schools, and lectured to Army Candidates for a period of about six years. During the last fifteen years had been engaged upon the Vegetable Oils, Gums, and latterly upon the Analysis and Structure of Steel. Is a Member of the Iron and Steel Institute, and Fellow of the Entomological Society.

F. E. Matthews.	A. Campion.
F. W. Harbord.	W. R. Hodgkinson.

A. H. Coote.

Hargreaves, Egerton, M.Sc.,

"Arthog," Garner's Lane, Davenport, Stockport.

Lecturer in Chemistry. 1. Student at Owens Coll., Manchester, 1901–4. In 1903 took Ord. Final, B.Sc. (Chem. and Physics), and in 1904, Final Hons. Chem. (1st Class). M.Sc. granted in 1907. 2. Full charge of Chemical Dept. at Stockport Technical School since 1907. 3. Desire to become a Member chiefly in order to keep in touch with modern chemical research.

Harold B. Dixon.	H. F. Coward.
W. H. Perkin.	J. L. Simonsen.
J. F. Thorpe.	Norman Smith.

Haws, John Frederick,

Parkfield Villa, Newton-by-Frankby, Cheshire.

Science Teacher. Student of Chemistry, Liverpool School of Science, 1898–1901; Ditto, Central Technical School, 1902–5. For 6½ years

with Professor J. Campbell Brown (as private secretary, 1903–7). Attended various day and evening classes in Chemistry at University (Liverpool), 1901–7; Summer Course (Chemistry), Royal College of Science, 1908. Assistant Demonstrator in Physiology and Hygiene, 1905, also Biology, 1906, and Botany, 1907, Central Technical School, Liverpool. 1st Class Hons. and King's Medal, Hygiene, 1907; Lecturer on Chemistry for Nat. Science Students, 1908.

J. Campbell Brown. G. T. Morgan.
Henry Bassett, jun. W. Collingwood Williams.
George Tate.

Hickinbotham, Reginald Vernon,
144, West Street, Maritzburg, Natal.

Analyst and Assayer. Six years at W. T. Henley's Telegraph Works as Assistant Chemist. Two years with Natal Paint Manufacturing Co., Ltd., Maritzburg, as Chemist and Manager, and four years as Public Analyst and Assayer.

R. L. Smith. R. J. Redding.
H. Russell Pitt. *H. Heron Smith.*
Wesley Lambert.

Hopkinson, Reginald, B.Sc. [Lond.].
Brimington House, Brimington, Nr. Chesterfield.

Science Teacher, Huntingdon Grammar School. Bachelor of Science (Chemistry), London University. Teacher of Chemistry for 6 years. Proceedings of Chemical Society required as an aid to research work.

J. H. Howgate. John T. Griffiths.
J. W. Shepherd. W. Carleton Williams.
Wm. Briggs.

Levy, Leonard Angelo,
60, Priory Road, West Hampstead, N.W.

Consulting Chemist. Chief chemist to Messrs. Sherard Cowper-Coles & Co., Ltd., 82, Victoria Street. B.Sc., Lond. (1st Class Honours in Chemistry). B.A. Cantab (1st Class, Parts I and II, Natural Science Tripos). A.I.C. "Some New Platinocyanides," *Trans. Chem. Soc.*, Vol. 89; "The Fluorescence of Platinocyanides," *Trans. Chem. Soc.*, Vol. 93. Two papers on Platinocyanides in *Proc. Camb. Phil. Soc.*

H. J. H. Fenton. W. J. Sell.
F. W. Dootson. H. O. Jones.
F. Ferraboschi.

Livsey, Harry,
54, Pemberton St., Old Trafford, Manchester.

Works Chemist at Messrs. J. & J. M. Worralls, Salford Branch of the English Velvet and Cord Dyers' Association. Employed as Chemist

at the above works for the last 9½ years, and formerly Chemist at the Littleborough Dyeing Co., 2½ years. Student in the Chemistry and Dyeing Depts., etc., of the Royal Salford Technical Institute, 5 years. Anxious to have the opportunity of keeping in touch with Chemical Research.

J. R. Appleyard. J. S. Broome.
B. Prentice. E. Clark.
E. Green. D. V. Hollingworth.

Metzger, Floyd J.,

Columbia University, New York City, N.Y.

Instructor in Analytical Chemistry. "On Cæsium Antimony Fluorides and other Halides of Antimony," *Am. Jour. Sci., XI*, 451; "On a Salt of Quadrivalent Antimony," *Am. Ch. J.*, **26**, 268; "On the Acid Nitrates," *Am. Ch. J.*, **26**, 271; "Thallic-thallous Nitrate," *Am. Ch. J.*, **26**, 277; "Separation of Tungstic and Silicic Acids," *Am. Ch. Soc.*, **23**, 356: with H. L. Wells. "A New Separation of Thorium, etc.," *Jour. Am. Chem. Soc.*, **24**, 901. "The Electrolytic Determination of Bismuth," with H. T. Beans, *Jour. Am. Chem. Soc.*, **30**, 589.

C. F. Chandler. Marston Taylor Bogert.
J. Livingston R. Morgan. Samuel A. Tucker.
Jas. S. C. Wells.

Müller, Robert,

Royal College of Science.

After the ordinary course of 3½ years at the "Polytechnikum" in Zürich, I succeeded in taking my Diploma examination. At present, I am working under Dr. Forster for my Ph.D.

James C. Philip. Chapman Jones.
G. T. Morgan. M. O. Forster.
Taylor Cook.

Okell, Frederick Leigh,

c/o Straits Trading Co., Singapore.

Analytical Chemist. Associate of the Institute of Chemistry. Chemical training received under Mr. W. F. Lowe, A.R.S.M., F.I.C., and at King's College, London, Sessions 1903–1905.

John M. Thomson. A. J. Greenaway.
Herbert Jackson. F. W. F. Arnaud.
Patrick H. Kirkaldy. Cecil Cooke Duncan.
W. F. Lowe. *L. C. Deverell.*

Owen, Robert Cecil,

89, Foregate St., Chester.

Chemist and Druggist and Science Lecturer. B.Sc. (London).

Lecturer in Science (chiefly Chemistry) to the Chester School of Science and to the Chester Society of Natural Science. Contributor to Pharmaceutical Papers.

John Bairstow. W. F. J. Shepheard.
G. Watmough Webster. John Welsh.

W. F. Lowe.

Rudolf, Norman Scott,
Bangalore, India.

Professor of Applied Chemistry at the Indian Institute of Science, Bangalore. M.Sc. (Victoria and Liverpool), F.I.C. 1893—1895 investigating chemistry of Indigo for Behar Planters, also in general analytical practice, holding appointment from Government of Bengal to examine potable waters on a fixed scale of fees. From 1895—1907 employed by Parke, Davis & Co., Manufacturing Chemists. In January, 1908, appointed to present position. Author of various papers published in Bulletin of Pharmacy, etc.

Morris W. Travers. A. W. Titherley.
J. Campbell Brown. Francis Francis.

Henry Bassett, jun.

Smith, Henry Llewellyn,
23, Ellingham Road, Shepherd's Bush, W.

Lecturer on Chemistry, King's College, London, and Lecturer on Applied Chemistry, Women's Department, King's College, London. B.Sc. (Manchester). Associate of the Institute of Chemistry. Part author, with Dr. Bone, of a paper on "The Thermal Decomposition of Formaldehyde and Acetaldehyde" (*Journal of the Chemical Society*, 1905, Vol. **87**).

John M. Thomson. W. H. Perkin.
Herbert Jackson. C. F. Cross.

Cecil H. Cribb.

Strohmenger, Arthur Percy,
Bridgebank, Harrow-on-the-Hill.

Analytical Chemist. Chemist to The Tudor Accumulator Co., Ltd., Hart Accumulator Co., Ltd., The Cape Asbestos Co., Ltd.

R. Meldola. E. W. Bealey.
John Castell-Evans. John Spiller.

Cecil H. Cribb.

Tate, Arthur Edwin,
Gladstone House, Salter Row, Pontefract.

Senior Science Master at King's School, Pontefract, since 1906,

and Junior Science Master (Chemistry) from 1905—1906. Science Master at Countess of Warwick's School for 2 years previous to the above appointment. Teacher of Chemistry in Evening Technical School, Pontefract.

P. Phillips Bedson. S. Hoare Collins.
F. C. Garrett. *J. T. Dunn.*
J. A. Smythe. *John Pattinson.*

Thomas, Oswald John Dalgatty,
65, Clarendon Gardens, Ilford, Essex.

Analytical Chemist. Student, Finsbury Technical Institute. Pupil to Mr. W. J. Dibdin, F.I.C., F.C.S. Cement and Gas Works Chemist. Agricultural Chemist.

Alex. H. Bennett. Robt. G. Grimwood.
F. H. Moore. *Wm. P. Skertchly.*
Thos. Macara.

Tilley, Vernon James,
"Linthorpe," Becmead Avenue, Streatham, S.W.

Analytical Chemist. Associate of the Institute of Chemistry. Desirous of keeping in touch with the latest progress in chemical literature.

John M. Thomson. Henry R. Lyell.
Tom R. Greenough. Reginald Howell.
Patrick H. Kirkaldy. William Stevenson.
Herbert Jackson. *Edward Bevan.*

Truelove, Charles William,
17, Tylney Road, Forest Gate, E.

Teacher. Student at East London College, 1904–1908. Student at Regent Street Polytechnic, 1907 to present time (engaged in Research Work). B.Sc. (Lond.). Desirous of keeping in touch with latest work in Chemistry.

J. T. Hewitt. H. Stanley Redgrove.
Clarence Smith. Frank E. Weston.
J. J. Fox. *H. R. Ellis.*
H. Mansfield. *W. H. Collier.*

Usher, Francis Lawry,
18, Clifton Park, Bristol.

Student. B.Sc. Lond. 1851 Exhibition Science Research Scholar, 1907–9. "Ueber die Löslichkeit von NO in wässerigen Lösungen von $FeSO_4$,$NiSO_4$,$CoSO_4$ and $MnCl_2$," *Zs. f. physik. Chem.*, **62** (1908), 622. Joint author of following: "On the Interaction of Arsenic Acid

with Hydrogen Sulphide in presence of Hydrochloric Acid," *J.C.S., Trans.*, **87** (1905), 1370. "On the Behaviour of Certain Substances at their Critical Temperatures," *Proc. Roy. Soc.*, **78**, *A*, 247. "The Mechanism of Carbon Assimilation in Green Plants," *Proc. Roy. Soc.*, (1906), **77**, *B*, 369. "The Mechanism of Carbon Assimilation in Green Plants: the Photolytic Decomposition of Carbon Dioxide *in vitro*," *Proc. Roy. Soc.*, **78**, *B*, 318 (1906).

William Ramsay. A. W. Stewart.
N. T. M. Wilsmore. R. W. Gray.
Edward C. Cyril Baly.

Walker, George Bilderbeck,

"Vale House," Trafalgar Road, Greenwich, S.E.

Pharmacist to the Greenwich Infirmary. Chemist. Member of the Pharmaceutical Society. Performs Analytical Work for the Greenwich Board of Guardians. Desirous of keeping in touch with the progress of Chemical Science and Research.

Arthur J. Dickinson. *W. R. Hodgkinson.*
Hermann C. T. Gardner. *O. Aubrey Elias.*
Arthur H. Coote. *Clement T. Rutter.*

Webster, John,

44, Holmewood Gardens, Brixton Hill, S.W.

Analytical Chemist. Studied Chemistry at Mason Univ. College, B'ham, under Prof. Percy F. Frankland. Assisted the late Sir Thos. Stevenson at Guy's Hospital (1901–1908). (Temporary) Public Analyst for the Boro' of St. Pancras (Aug.–Oct. 1908). Fellow of the Institute of Chemistry. Demonstrator in Pathological Chemistry and Assistant Chemical Pathologist at St. Mary's Hospital, W. (at the present time).

Arthur P. Luff. George Senter.
W. H. Willcox. R. Bodmer.
G. Roche Lynch.

Wilson, Robert William,

2, Parade, Aldersbrook Road, Manor Park, E.

Lecturer on Chemistry, Technical College, East Ham. Board of Education Certificates, Stage III, Inorganic and Organic. Have carried out Research work with A. E. Dunstan, B.Sc. on (1) "Viscosity of Liquid Mixtures—H_2SO_4 and H_2O"; (2) "Viscosity of Fuming Sulphuric Acid," *Trans.*, 1907 and 1908. At present engaged in Research on "The Existence of Double Salt Complexes in Solution."

W. H. Barker. George Young.
A. E. Dunstan. T. P. Hilditch.
C. Schlienger.

The following Certificate has been authorised for presentation to Ballot by the Council under Bye-law I (3):

Bletcher, Henry Ernest John,
Winnipeg, Manitoba.

Professor of Chemistry. Have been for eighteen years a student and teacher of Chemistry, and for the past nine years have been Professor of Chemistry in the Manitoba College of Pharmacy, which is affiliated with the University of Manitoba.

Matthew A. Parker. *G. G. Henderson.*
E. B. Shuttleworth. *William S. Denham.*

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 14/5/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 356.

Thursday, May 6th, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

Messrs. H. C. Duckworth and I. H. Zortman were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Harold Edward Annett, B.Sc., Imperial Research Institute, Pusa, Behar, Bengal, India.
Harold Arnfield, Peak Lodge, Buxton Road, Stockport.
Alfred Charles Glyn Egerton, B.Sc., Chilton House, Thame, Oxon.
Harry Essex, jun., 23, Bescot Street, Walsall.
Andrew Sneddon Matchet, 13, Bute Gardens, Cathcart, N.B.
Norman Picton, B.Sc., Ph.D., 4, Pembroke Square, Kensington, W.
Herbert Charles Resker, B.A., The Sugar Works, Cossipore, Calcutta, India.
Barth. Frere Sawbridge, B.A., Thelnetham Rectory, Diss, Norfolk.
Harry Sampson Wills, 59, Caldecott Road, Denmark Hill, S.E.
George James Woods, 2, Wellmeadow Road, Lewisham, S.E.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected:

Hugh Garner Bennett, M.Sc.
Albert Riley Blackburn, B.Sc.
Henry Ernest John Bletcher.
Frank Playfair Burt, B.Sc.
Walter Campbell.
Howard Alfred Caulkin, B.Sc.
John Henry Chew.
George Clarke.

Reginald Cyril Herbert Cooke.
George Stanley Cooper.
Daniel Little Couch.
Edward Gordon Couzens, B.Sc.
Henry Jermain Maude Creighton, M.A.
Philip Henry Crewe.
Francis Clifford Dyche-Teague, B.Sc.
William Fowler.
Charles James Grist.
Egerton Hargreaves, M.Sc.
John Frederick Haws.
Reginald Vernon Hickinbotham.
Reginald Hopkinson, B.Sc.
Leonard Angelo Levy, B.A., B.Sc.
Harry Livsey.
Floyd J. Metzger.
Robert Müller.
Frederick Leigh Okell.
Robert Cecil Owen, B.Sc.
Norman Scott Rudolf, M.Sc.
Henry Llewellyn Smith, B.Sc.
Arthur Percy Strohmenger.
Arthur Edwin Tate.
Oswald John Dalgatty Thomas.
Vernon James Tilley.
Charles William Truelove, B.Sc.
Francis Lawry Usher, B.Sc.
George Bilderbeck Walker.
John Webster.
Robert William Wilson.

Of the following papers, those marked * were read :

***115. "The absorption spectra of the nitrates in relation to the ionic theory." By Edward Charles Cyril Baly, Katharine Alice Burke, and Effie Gwendoline Marsden.**

The absorption spectra have been examined of nitric acid and lithium, ammonium, and silver nitrates dissolved in alcohol and in water and in various mixtures of these solvents. A comparison between the persistencies of the absorption band shown by $N/10$-solutions of lithium and ammonium nitrates shows that considerable variations occur as the percentage of water in the solvent is increased. For example, when the solvent contains 3 per cent. of water a great decrease in the persistence of the absorption band is obtained as compared with that observed in pure alcohol and in alcohol containing 10 per cent. of water. On the other hand, the electrical conductivities of the $N/10$-solutions do not show any such variations, but only a steady increase with increase of water in the solvent. If, however, the limiting conductivities of the solutions be observed, it is found that a minimum is obtained when the solvent contains 3 per cent. of water. Nitric acid differs from the metallic nitrates in that it shows no absorption band and possesses very small electrical conductivity in pure alcoholic solution. The absorption band is developed, however, and the conductivity greatly increased with addition of water to the solvent. The limiting conductivity of the nitric acid solutions also shows a minimum with 3 per cent. of water in the solvent. The results afford strong support to the theory of hydrated ions, the decrease in limiting conductivity and the absorption band observed with the solvent containing 3 per cent. of water being doubtless due to the hydration taking place.

Discussion.

Dr. Senter asked if there was any evidence of a connexion between the viscosity of the (mixed) solvent and the limiting molecular conductivity of the salts (compare Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 217).

Mr. Baly said that the viscosity of the solvent seemed to exert only a very small influence. A mixture of alcohol and water in equal proportions showed a maximum viscosity, and although there was a minimum in the limiting conductivity of lithium nitrate near this point, neither silver nitrate nor ammonium nitrate showed any such minimum.

*116. **"Studies in the camphane series. Part XXVI. Aryl derivatives of iminocamphor." By Martin Onslow Forster and Tom Thornley.**

By condensing camphorquinone with aniline and some of its derivatives, aryliminocamphors have been obtained and are found to possess unusually high specific and molecular rotatory power. Reduction of these compounds leads to the corresponding derivatives of aminocamphor, and is accompanied by profound depression of optical activity.

Discussion.

Mr. P. W. Robertson asked whether the coloured compound investigated dissolved with different intensities in different solvents, and if so, whether any relationship had been observed between the intensity of colour and the magnitude of the specific rotation.

*117. **"Substituted dihydrobenzenes. Part III. The so-called 1 : 1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene of Harries and Antoni." By Arthur William Crossley and Nora Renouf.**

It was shown that the hydrocarbon described by Harries and Antoni (*Annalen*, 1903, **328**, 88) as 1 : 1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene is in reality a mixture of the *cyclo*hexadienes with the two methyl groups in the 1 : 2- and 1 : 3-positions, and probably does not contain any 1 : 1-dimethyl*cyclo*hexadiene.

*118. **"Diethoxythioxan; a relation between the refractive power and chemical activity of some sulphur compounds." By Hans Thacher Clarke and Samuel Smiles.**

The interaction of sodium sulphide and chloroacetal in alcoholic solution furnishes acetal sulphide, which, on treatment with mineral

acid, yields the cyclic sulphide, *diethoxythioxan*. The reactivity of the sulphur in the latter compound has been qualitatively studied, and it is found to be abnormally low in comparison with that of the same element in acetal sulphide, benzyl sulphide, or saturated aliphatic sulphides. The authors consider that this depressed activity cannot be satisfactorily explained by steric hindrance, and, instead, offer the hypothesis that the residual affinities of the unsaturated cyclic sulphur and oxygen partly saturate one another. A similar explanation may be applied to other compounds containing bivalent sulphur of abnormally low activity, for example, thiophen and phenyl sulphide. The refractivity of these sulphur compounds also has been studied, and it was shown that a subnormal reactivity is accompanied by abnormal refractive power. The thioxan derivative appears to possess a slight optical anomaly.

Discussion.

Dr. Smiles, in reply to Mr. Baly, stated that attempts made with the object of preparing a hydrochloride of diethoxythioxan had been unsuccessful. No indications of the substance having the structure of a hydroxytetrahydrothiophen, as suggested by Dr. Forster, had been found, since acyl derivatives were unobtainable.

In reply to the President's question as to the action of oxidising agents, hydrogen dioxide was without action, but hot concentrated nitric acid destroyed the substance, sulphuric acid being formed.

119. "The affinity constants of hydroxy- and alkyloxy-acids." By Alexander Findlay, William Ernest Stephen Turner, and Gertrude Emily Owen.

The affinity constants of phenylmethoxy-, phenylethoxy-, and phenylpropoxy-acetic acids and of α- and β-hydroxy-β-phenylpropionic acids have been determined at 25°. The values of the constant $100k$ were found equal to 0·074, 0·053, 0·048, 0·019, and 0·0040 respectively.

120. "The chlorination of acetanilide." By William Jacob Jones and Kennedy Joseph Previté Orton.

When chlorinated by bleaching powder solution in acetic acid solution, acetanilide is converted into a mixture of *o*- and *p*-chloroacetanilides, of which the ortho-compound forms about 45 per cent., and not, as believed heretofore, less than 10 per cent. If the concentration of the acetic acid is less than 2 per cent., acetylchloroaminobenzene is formed together with the two chloroacetanilides; when the

acetic acid is diluted to 0·25 per cent., the chloroamine forms the chief product.

The transformation of the acetylchloroaminobenzene yields a mixture of the isomeric chloroacetanilides in the same proportion. Chlorination of acetanilide by chlorine in glacial acetic acid solution gives a mixture of the two anilides, in which 30 to 32 per cent. of the ortho-derivative is present.

121. "Esterification constants of substituted acrylic acids. Part IV." By John Joseph Sudborough and Morton James Pryce Davies.

The constants, $E^{15°}_{MeOH}$, have been determined for the following acids: Acrylic, crotonic, α-methylacrylic, ββ-dimethylacrylic, angelic, tiglic, trimethylacrylic, *iso*butyric, α-methylbutyric, *iso*valeric, αβ-dimethylbutyric. The results indicate the retarding effect of the methyl groups and also establish the retarding effect of the double linking in the αβ-position. The most remarkable point is that ββ-dimethylacrylic acid is esterified less readily than α-methylacrylic acid or tiglic acid.

122. "The action of the halogens on aromatic hydrazines." By Frederick Daniel Chattaway.

From the behaviour of the primary aromatic hydrazines when oxidised, it seemed likely that evidence of the formation of the mono-*N*-halogen substituted derivatives, which should be the first products of the interaction of primary aromatic hydrazines and any halogen, would be obtained if the reactions were carried out in presence of alkalis. Such compounds in presence of alkalis would be unstable, and might be expected to decompose into nitrogen, halogen hydride, and hydrocarbons. *N*-Dihalogen substituted derivatives, corresponding with the halogen acid additive products of diazonium salts, might be formed in small amount under favourable conditions and similarly decompose, yielding a monohalogen-substituted hydrocarbon. These expectations have been completely realised. When chlorine or bromine is brought into contact with a primary aromatic hydrazine in presence of potassium or sodium hydroxide, very vigorous action takes place, nitrogen is freely evolved, and the $\cdot NH \cdot NH_2$ group is replaced by hydrogen; for example, by the action of bromine on phenylhydrazine, *p*-bromophenylhydrazine, *o*-tolylhydrazine, and *p*-tolylhydrazine, there are produced benzene, *p*-bromobenzene, and toluene respectively. Any theory which attempts to explain the action of the halogens on primary aromatic hydrazines must therefore account for the produc-

tion of hydrocarbons, mono-, di-, tri-, and tetra-substituted hydrocarbons, azo-derivatives, azoimides, hydrocarbons of the diphenyl series, diazonium salts substituted and unsubstituted in the aromatic nucleus, and the so-called diazonium perbromides.

It was explained how the complicated changes, which result in the formation of so many substances of such very different constitutions, all depend on a progressive substitution of hydrogen attached to the nitrogen, thus:

$$\begin{matrix} R\cdot N\cdot H \\ H\cdot N\cdot H \end{matrix} \rightarrow \begin{matrix} R\cdot N\cdot H \\ H\cdot N\cdot X \end{matrix} \rightarrow \begin{matrix} R\cdot N\cdot X \\ X\cdot N\cdot H \end{matrix} \rightarrow \begin{matrix} R\cdot N\cdot X \\ X\cdot N\cdot X' \end{matrix}$$

followed by a breaking down or intramolecular rearrangement of the *N*-halogen-substituted hydrazines thereby produced.

123. "The retarding effect of oxygen on the rate of interaction of chlorine and hydrogen." By David Leonard Chapman and Patrick Sarsfield MacMahon.

The authors have shown that when a moist mixture of chlorine and hydrogen containing a known amount of oxygen is exposed to light of constant intensity, the rate of formation of hydrogen chloride is, to a first approximation, inversely proportional to the amount of oxygen present. It is concluded from this result that the sensitiveness of a mixture of chlorine and hydrogen from which all oxygen had been removed would be infinite. The above quantitative relation was shown to be in harmony with the theory of inhibition advanced by Burgess and Chapman (*Trans.*, 1906, **89**, 1433).

124. "The colour of aqueous solutions of violuric acid." By Frederick George Donnan and Wilhelm Schneider.

Experiments were described which show that the conclusion of W. N. Hartley (*Trans.*, 1905, **87**, 1797), that pure aqueous solutions of violuric acid are colourless, is erroneous.

125. "An examination of irritant woods. Part I. Chloroxylonine from East Indian satinwood." By Samuel James Manson Auld.

From East Indian satinwood, derived from *Chloroxylon swietenia*, which has been reported to possess irritant properties, have been separated calcium oxalate, a peculiar protein compound, two inert resins, a fixed oil, and an alkaloid, $C_{22}H_{23}O_7N$. As the alkaloid cannot be identified with any known base, it is proposed to call it *chloroxylonine*.

Chloroxylonine is a weak monoacidic base, and several of its salts have been prepared and characterised. It melts at 182—183°, contains four methoxyl groups, and is lævorotatory ($[\alpha]_D^{18}$ – 9°18′). The physiological action of chloroxylonine is being investigated by Prof. Cash, of Aberdeen, and in certain circumstances it seems capable of causing dermatitis similar to that ascribed to the wood itself.

126. "Diazohydroxylamino-compounds and the influence of substituting groups on the stability of their molecules. Part II." By Norman Leslie Gebhard and Herbert Bryan Thompson.

The various diazohydroxylamino-compounds, prepared as described in the previous paper (*Trans.*, 1909, **95**, 767), have been examined with a view to determine the influence, due to position in the molecule, which the various substituting groups have on the stability of the compound considered. The action of bromine dissolved in an organic solvent, besides being a decomposing one, is of a substituting nature, and consequently of little use in determining the object in view; several new diazohydroxylamino-compounds were, however, prepared by its means. The action of hydrochloric acid in an organic solvent under comparable conditions for the various series of isomeric substitution products was also investigated; it was found that the nitro-, bromo-, and carbethoxy-groups (but not the methyl group), when present in the ortho-position, greatly increased the stability, but as soon as the substituting group entered the meta- or para-positions the stability of the molecule decreased enormously.

127. "A new method of preparing camphoric anhydride." By John Percy Edgerton.

When camphoric acid is treated with chlorosulphonic acid a vigorous reaction takes place according to the equation:

$$C_8H_{14}(CO_2H)_2 + HSO_3Cl = C_8H_{14}\begin{matrix}CO\\CO\end{matrix}O + H_2SO_4 + HCl,$$

the principal product being camphoric anhydride, which can be quickly prepared as follows: One hundred grams of finely powdered camphoric acid are placed in a capacious flask fitted with a drying tube containing calcium chloride, and 33 c.c. of chlorosulphonic acid are added; the mixture is then warmed on the water-bath, a further quantity of 16·5 c.c. of chlorosulphonic acid is added, and the whole again warmed for about half an hour until the evolution of gas has practically ceased. The mass is then mixed with water, filtered

through glass wool, and washed until free from acid. The camphoric anhydride crystallises from methylated spirit in fine needles, which, if not quite pure, can be obtained pure by a second crystallisation.

128. "The action of phosphorus pentachloride on benzamide." By Arthur Walsh Titherley and Elizabeth Worrall.

In the action of phosphorus pentachloride on benzamide different results are obtained according to whether the action takes place (1) in the cold without a solvent, or (2) in the cold with a solvent, or at 50° with or without a solvent. In (1) the result appears to be a mixture of phosphoryl chloride and α-chlorobenzimide, $C_6H_5\cdot CCl{:}NH$, which gradually passes into benzonitrile and could not be isolated; in (2) *αα*-dichlorobenzylphosphamic chloride, $C_6H_5\cdot CCl_2\cdot NH\cdot POCl_2$, is formed, which immediately loses hydrogen chloride, yielding *α-chlorobenzylidenephosphamic chloride*, $C_6H_5\cdot CCl{:}N\cdot POCl_2$, as an oil which solidified at low temperatures. The latter compound is comparatively stable at 50°, but decomposes at higher temperatures into benzonitrile and phosphoryl chloride; on exposure to atmospheric moisture, it yields fine transparent crystals of *benzoylphosphamic chloride*,

$$C_6H_5\cdot C(OH){:}N\cdot POCl_2 \rightleftarrows C_6H_5\cdot CO\cdot NH\cdot POCl_2$$

(m. p. 115°), which is practically unaffected by cold water. By treatment with aniline, α-chlorobenzylidenephosphamic chloride yields *phenyliminophosphorylphenylbenzamidine*, $C_6H_5\cdot C(NHPh){:}N\cdot PO{:}NPh$ (m. p. 227—228°).

Benzoylphosphamic chloride on treatment with aniline yields *phenyliminophosphorylbenzamide*,

$$C_6H_5\cdot CO\cdot NH\cdot PO{:}NPh \rightleftarrows C_6H_5\cdot C(OH){:}N\cdot PO{:}NPh$$

(m. p. 226°), which is soluble in sodium hydroxide, or *benzoylaminoanilinophosphoryl chloride*, $C_6H_5\cdot CO\cdot NH\cdot POCl\cdot NHPh$ (m. p. 176°), according to the conditions of the reaction. The latter compound passes into the former by treatment with aniline, and does not yield the expected dianilino-derivative.

Benzoylphosphamic chloride readily undergoes replacement of the two chlorine atoms by hydroxyl on treatment with water in acetone solution, yielding *benzoylphosphamic acid*, $C_6H_5\cdot CO\cdot NH\cdot PO(OH)_2$ (m. p. 157—158°), which is readily soluble in water, and forms salts. The acid is rapidly decomposed by water at 100°, yielding phosphoric acid and benzamide, which crystallises out on cooling.

129. "Estimation of iron by permanganate in the presence of hydrogen chloride." By John Albert Newton Friend.

The author draws attention to the fact that the rate at which the permanganate is added to the ferrous solution greatly affects the

value of the titration. It is suggested that the reaction takes place in two stages. First, a partial reduction resulting in the oxidation of some of the iron, and the formation of an unstable perchloride of manganese. The latter substance then oxidises the ferrous iron according to the equation:

$$MnCl_{(x+2)} + xFeCl_2 \longrightarrow MnCl_2 + xFeCl_3$$

until equilibrium is established.

If the directions given are rigidly adhered to, fairly accurate estimations of iron may be obtained in the presence of *N*/4-hydrochloric acid.

130. "**Contributions to the chemistry of the terpenes. Part V. The action of chromyl chloride on terpinene and on limonene.**" **By George Gerald Henderson and William Cameron.**

When chromyl chloride (2 mols.), largely diluted with carbon disulphide, is added to a similar solution of terpinene (1 mol.), a brown solid is formed which is decomposed by water, yielding a solution of chromic chloride and a brown, oily liquid. The liquid oxidation product contains small quantities of cymene and of a *ketone* of the formula $C_9H_{12}O$, but is mainly composed of *α*-*p*-tolylpropaldehyde, $C_6H_4Me{\cdot}CHMe{\cdot}CHO$, and *p*-tolyl methyl ketone, $COMe{\cdot}C_6H_4Me$, both of which are derivatives of cymene. Hence the behaviour of terpinene towards chromyl chloride is different from that of pinene and of camphene, for whilst each of the latter hydrocarbons yields an additive product, $C_{10}H_{16},2CrO_2Cl_2$, terpinene, on the other hand, is for the most part first oxidised to cymene, which then forms the compound $C_{10}H_{14},2CrO_2Cl_2$, from which the aldehyde and the ketone are produced by the action of water.

It has also been found that the aldehyde and the ketone formerly prepared from limonene in a similar manner (*Trans.*, 1907, **91**, 1871) are largely composed of *α*-*p*-tolylpropaldehyde and *p*-tolyl methyl ketone respectively, and therefore that limonene must likewise undergo at least partial oxidation to cymene when attacked by chromyl chloride under the conditions described.

131. "**The influence of solvents on the rotation of optically active compounds. Part XV. Mixed solvents.**" **By Thomas Stewart Patterson and Harvey Hugh Montgomerie.**

The influence of two pairs of solvents on the rotation of an active compound was described, and the results were discussed in connexion with the heat of mixture of the various compounds concerned, and also with reference to the discrimination of compounds in solutions.

132. "Optically active reduced naphthoic acids. Part IV. Comparison of the rotatory powers of the di- and tetra-hydronaphthoic acids with those of phenylallylacetic, α-phenylvaleric, β-phenyl-α-ethyl- and β-phenyl-α-methyl-propionic acids." By Robert Howson Pickard and Joseph Yates.

A description was given of the resolution of five racemic acids by the fractional crystallisation of their *l*-menthylamine salts. The principal experimental results are recorded in the following table:

	Acid.					Menthylamine salt.	
Dextrorotatory acids.	M. p.	$[M]_D$ at 20°.	$[M]_D$ in $CHCl_3$.	$[M]_D$ in C_6H_6.	$[M]_D$ of sodium salt in H_2O.	M. p.	$[M]_D$ in ethyl alcohol.
Δ^3-Dihydro-2-naphthoic ...	101° below	—	+276·2°	+317·0°	+309·0°	143—144°	+251·6°
Phenylallylacetic	10°	—	148·9	181·6	40·2	145	−2·7
α-Phenylvaleric	,,	+128·3	104·7	140·7	5·0	141	−58·4
β-Phenyl-α-ethylpropionic	,,	—	68·3	73·0	100·7	137	−22·3
β-Phenyl-α methylpropionic	,,	37·1	45·5	44·4	66·8	143	+54·6

133. "The influence of hydroxy- and alkyloxy-groups on the velocity of saponification. Part II." By Alexander Findlay and Evelyn Marion Hickmans.

The velocities of saponification of ethyl glycollate, lactate, α-hydroxy-β-phenylpropionate, γ-hydroxy-γ-phenylbutyrate, phenylpropionate, propionate, β-hydroxy-β-phenylpropionate, and of methyl phenylacetate have been determined. The values of the saponification constant obtained for these esters were 75, 63·5, 40·1, 16·5, 6·9, 5·3, 4·9, 27·4 respectively. From these numbers it is found that the introduction of a phenyl group accelerates the velocity of saponification, except when the ester contains the hydroxyl group. In this case, introduction of a phenyl group lowers the velocity of saponification (for example, ethyl mandelate and ethyl glycollate). Introduction of an hydroxyl group increases the saponification constant to nearly twelve times its value in the case of esters not containing the phenyl group, but to only five to six times its value in the case of phenylated esters. A comparison of the saponification constants of the ethyl esters with the affinity constants of the corresponding acids shows that there is no general relationship between the two magnitudes.

134. "**Apparatus for experiments at high temperatures and pressures, and its application to the study of carbon. (A correction).**" **By Richard Threlfall.**

The author recently described an experiment (*Trans.*, 1908, **93**, 1333) in which graphite was forced through a narrow tube by a comparatively small pressure—negligible in comparison with the pressures under which the property of the fluidity of graphite was employed to transmit pressure. The experiment there described can be repeated as often as desired, but the inference that pressure can be transmitted in all circumstances without any appreciable loss of head by crystalline graphite is wrong. Further experience has shown that when graphite flows it does not obey the laws regulating the flow of liquids, but that the fluidity of graphite is a function of the absolute pressure to which it is exposed. Under high pressures the graphite consolidates, and in this state transmits pressure very badly. For instance, in the experiment described (*loc. cit.*), it is now known that rapid flow took place under a pressure of a few hundred pounds per square inch—the graphite flowing freely into the air. When, however, the graphite, otherwise under similar conditions, was employed to force a pointed piston of hard steel against a soft steel plate, and pressures of 50 to 100 tons per square inch were employed for the purpose, a loss of head of many tons per square inch was found. The observation was made by measuring the depth to which the pointed piston entered the steel plate, and then causing it to penetrate to the same depth by direct pressure. In most of the experiments described in the paper referred to, the graphite flowed into a bath of molten magnesia through a very short neck of unmelted tube, and consequently the experimental results quoted are probably little or not at all affected by the error involved in supposing that graphite, when it flows, obeys the ordinary laws of flow of liquids. Some preliminary experiments indicate that cold lead flowing under high pressure is much more truly a fluid than crystalline graphite.

135. "**Experiments on the constitution of the aloins. Part I.**" **By Robert Robinson and John Lionel Simonsen.**

The authors communicated the results of some further experiments on the nature of rhein, a preliminary note of which has already appeared (*Proc.*, 1909, **26**, 76).

136. "The constitution of the salts of barbituric acid." By John Kerfoot Wood and Emma Alexander Anderson.

The authors have shown that by the action of acetic anhydride on a mixture of carbamide and malonic acid, *ureidomalonamide* is formed, together with barbituric acid and an apparently complex substance, the constitution of which has not been established. Ureidomalonamide is a white, very sparingly soluble substance, which, on treatment with sodium hydroxide, is converted into sodium barbiturate. This action shows that the constitution of the salts of barbituric acid is represented by the general formula $MO\cdot C\begin{matrix}CH\cdot CO\\NH\cdot CO\end{matrix}>NH$, where M is a univalent metal. Theoretical considerations leading to a similar conclusion were also discussed.

137. "The estimation of carbonates in presence of nitrites, sulphides or sulphites by means of potassium dichromate." By Ernest Robert Marle.

It was proved that soluble carbonates and carbonates of bases which form soluble chromates are quantitatively decomposed by aqueous potassium dichromate. The action of potassium dichromate on nitrites has been investigated. On distillation with dichromate, a nitrite yields nitrous acid, although the mixed solution apparently contains no free nitrous acid. The yield of nitrous acid increases with the concentration of the nitrite, but is almost independent of that of the dichromate.

Prolonged distillation, either adding water at the rate at which the liquid distils, or making the solution up to its original volume after, say, 100 c.c. has distilled over, gives 60—70 per cent. of the nitrite as nitrous acid. The residual nitrite in the flask is estimated, and the loss of 10—15 per cent. is accounted for by the decomposition of nitrous acid into nitric acid and nitric oxide, some of the nitric oxide remaining dissolved in the dichromate solution.

An apparatus was described with which carbonates can be estimated in the presence of nitrites, the mixture being distilled with dichromate under reflux. The carbon dioxide is thus freed from nitrous acid, and the nitric oxide formed is negligible. The method is found to give accurate results.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Clowes, *Frank,* and **Coleman,** *J. Bernard.* Elementary practical chemistry. Part II. Analytical chemistry. 6th edition. pp. xv + 241. ill. London 1909. (*Recd.* 7/4/09.)
From the Publishers: Messrs. J. & A. Churchill.

Keane, *Charles Alexander.* Modern organic chemistry. pp. xv + 503. ill. London 1909. (*Recd.* 15/4/09.) From the Author.

Mees, *C. E. Kenneth.* The photography of coloured objects. pp. vi + 69. ill. Croydon 1909. (*Recd.* 15/4/09.)
From the Author.

Miller, *Wilhelm von,* und **Kiliani,** *Heinrich.* Kurzes Lehrbuch der analytischen Chemie. 6th edition. pp. xi + 643. ill. München 1909. (*Recd.* 14/4/09.) From Professor H. Kiliani.

Parry, *L.* Systematic treatment of metalliferous waste. pp. 121. London [1909]. (*Recd.* 17/4/09.)
From the Publisher: *The Mining Journal.*

Sudborough, *John Joseph,* and **James,** *T. Campbell.* Practical organic chemistry. pp. xviii + 378. ill. London 1909. (*Recd.* 16/4/09.) From the Publishers: Messrs. Blackie & Son.

II. *By Purchase.*

Calmette, *A.* Recherches sur l'épuration biologique et chimique des eaux d'égout. Vols. 3 & 4. pp. v + 274, iv + 214. ill. Paris 1908–09. (*Recd.* 24/4/09.)

Rupe, *Hans.* Die Chemie der natürlichen Farbstoffe. Teil II. (Bolley's *Handbuch,* 61.) pp. ix + 236. Braunschweig 1909. (*Recd.* 31/3/09.)

Witt, *Otto N.,* and **Lehmann,** *Ludwig.* Chemische Technologie der Gespinnstfasern. Lieferung 4. (Bolley's *Handbuch,* 67.) pp. 577—770. Braunschweig 1909. (*Recd.* 31/3/09.)

Wright, *Herbert.* Hevea Brasiliensis, or Para rubber: Its botany, cultivation, chemistry and diseases. 3rd edition. pp. xvii + 204. ill. Colombo 1908. (*Recd.* 27/4/09.)

Wurtz, *Adolf.* Abhandlung über die Glycole oder zweiatomige Alkohole und über das Aethylenoxyd als Bindeglied zwischen organischer und Mineralchemie. Aus dem Französischen übersetzt und mit Anmerkungen versehen von *M.* u. *A.* **Ladenburg.** (Ostwald's *Klassiker,* No. 170.) pp. 96. Leipzig 1909. (*Recd.* 24/4/09.)

III. *Pamphlets.*

Bein, *W.* Zur Ausdehnung des Aethylaethers und einiger Mischungen des aethers mit Aethylalkohol. (From the *Abhandl. K. Normal-Eichungskom,* 1908, **7**.)

Dezani, *Serafino.* Le basi proteiche contenute nello sperma e nelle ovaie del tonno ed i loro prodotti idrolitici. (From the *Giorn. R. Accad. Med. Torino,* 1908, **14**.)

Fermor, *L. Leigh.* Note on a group of Manganates, comprising Hollandite, Psilomelane, and Coronadite. (From the *Records, Geol. Survey of India,* 1908, **36**.)

Fischer, *H. W.* Untersuchungen über Metallhydroxyde. pp. 80. Breslau 1907.

Grünwald, *Hermann Friedrich.* Ueber die Lebenswichtigkeit der Chloride für den Organismus. (From the *Zentr. Physiol.,* 1908, **22**.)

Strauss, *Eduard.* Notiz zum Nachweis des Urobilins im Harn. (From the *Münch. med. Woch.,* 1908.)

WOLCOTT GIBBS MEMORIAL LECTURE.

The above lecture will be delivered by Professor Frank Wigglesworth Clarke at the Ordinary Scientific Meeting on Thursday, June 3rd, at 8.30 p.m.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, June 7th, 1909.

All persons who received grants in June, 1908, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Tuesday, June 1st.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

At the next Ordinary Meeting on **Thursday**, May **20th**, 1909, at **8.30** p.m., the following papers will be communicated:

"The action of nitric acid on the ethers of aromatic hydroxyaldehydes." By A. H. Salway.

"Isolation and synthesis of *p*-hydroxyphenylethylamine, a water-soluble active principle of ergot." By G. Barger.

"Nitrodi-*o*-xylyl. (Nitrotetramethyldiphenyl.) Preliminary note." By A. W. Crossley and C. H. Hampshire.

"Ammonium perhalides." By F. D. Chattaway.

"Studies in asymmetric synthesis. Part VIII. The asymmetric synthesis of *l*-mandelic acid." By A. McKenzie and H. B. P. Humphries.

"Note on the condensation of acetone and hippuric acid." By W. H. Perkin and J. L. Simonsen.

"Sodium sulphite." By H. Hartley and W. H. Barrett.

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OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 357.

Thursday, May 20th, 1909, at 8.30 p.m., Sir JAMES DEWAR, F.R.S., Past-President, in the Chair.

Messrs. F. P. Burt, R. C. H. Cooke, G. S. Cooper, and F. L. Usher were formally admitted Fellows of the Society.

The CHAIRMAN announced that the Council had voted the sum of £10 towards the International Memorial now being organised to commemorate the contributions of Amedeo Avogadro to chemical and and physical science.

It was stated also that the Society have become indebted to the Society of Dyers and Colourists for a bronze reproduction of a plaque by Mr. F. W. Pomeroy, R.A., representing the late Sir William Perkin.

Certificates were read for the first time in favour of Messrs. :—

John Gunning Moore Dunlop, St. Helen's, Holywood, Belfast.
Oswald Farquhar Kirby, M.A., B.Sc., 14, Wellclose Mount, Leeds.
Fred Robinson, B.A., B.Sc., Broadway, Skerton, Lancaster.

Of the following papers, those marked * were read :

*138. "Thio-oxalates." (Preliminary note).

By Humphrey Owen Jones and Hubert Sanderson Tasker.

The esters of dithio-oxalic acid are readily prepared by the action of alkyl hydrosulphides on oxalyl chloride; the dimethyl, diethyl, and

diphenyl esters are crystalline, and show a distinct yellow colour (the diphenyl compound is a bright sulphur-yellow).

These esters are decomposed by hot potassium hydroxide solutions into potassium oxalate and alkyl hydrosulphide, but when heated with a concentrated alcoholic solution of potassium hydrosulphide a white solid separated, which was found to be *potassium dithio-oxalate*, $(KSCO)_2$. This salt is white and crystalline, and is very soluble in water, giving a yellow solution, from which it separates in colourless prisms when evaporated on the water-bath. The salt gives intense colours with solutions of certain metallic salts, and precipitates with others; some of these precipitates decompose on heating, yielding the sulphide of the metal. The most striking reactions are those given with solutions of nickel and cobalt salts, the former give an intense magenta colour, the latter a deep brown colour, in both cases so intense as to be visible in solutions containing one part of the metal in 8,000,000 parts of solution.

The coloured compound formed with nickel can readily be obtained in small, black, lustrous needles, resembling small crystals of potassium permanganate; these were found to have the composition required by the formula $C_4O_4S_4K_2Ni$. Solutions of this salt and the cobalt salt are stable to acids, and the metals are only precipitated very slowly from them by the addition of potassium hydrosulphide or hydroxide.

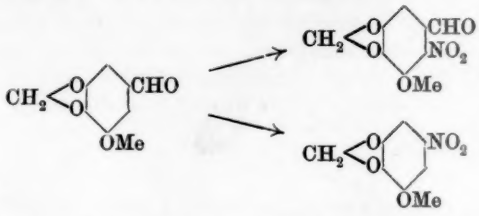
Potassium monothio-oxalate is prepared by the action of alcoholic potassium hydrosulphide on diethyl monothio-oxalate, $(COSEt{\cdot}CO_2Et)$, and separates slowly in white needles, which contain one molecule of water of crystallisation. This salt is also very soluble in water, but gives a colourless solution; the solution decomposes on addition of acid, and gives colours and precipitates with metallic salts which are very similar to those given by the dithio-oxalate, but the insoluble salts are in this case more readily decomposed.

The corresponding acids are unstable, and have not yet been isolated in the pure state.

***139. "The action of nitric acid on the ethers of aromatic hydroxyaldehydes." By Arthur Henry Salway.**

The author has shown that when myristicinaldehyde is acted on by nitric acid (sp. gr. 1·41) at 0°, part of the aldehyde is directly nitrated, whilst the remainder undergoes nitration with the elimination of the aldehyde group, the products of the reaction being nitromyristicinaldehyde and 5-nitro-1-methoxy-2:3-methylenedioxybenzene. It was also shown, by determining the position of the nitro-group, that the formation of the latter compound is due to the direct substitution of

the aldehyde group by the nitro-group. The action of nitric acid on myristicinaldehyde is represented, therefore, as follows :



On investigating the action of nitric acid on piperonal, vanillin methyl ether, and anisaldehyde, it was found that the above transformation is common to the ethers of aromatic hydroxyaldehydes, and that the accumulation of oxyalkyl groups in the molecule enhances the readiness with which the aldehyde group is eliminated on nitration.

Discussion.

Dr. Morgan remarked that the author's hypothesis of the formation of an additive compound with aldehyde and nitric acid preceding the replacement of the aldehyde group by nitroxyl is confirmed by the fact that aldehydes and ketones both furnish nitrates which may often be obtained crystalline. Camphor nitrate has long been known, and benzaldehyde nitrate has recently been isolated (D.R.-P. 206695 and *Abstr.*, 1909, i, 238).

*140. "Some physical properties of radium emanation." By Robert Whytlaw Gray and Sir William Ramsay, K.C.B.

The atomic weights of the inactive gases are: helium, 4; neon, 20; argon, 40; krypton, 83, and xenon, 131. The differences are respectively 16, 20, 43, and 48. Differences of 44×2 are to be found between the atomic weights of antimony and bismuth, and of barium and radium; it is therefore to be expected that the element following xenon in the periodic table should have the atomic weight 175; the subsequent element, 219; and possibly an element of still higher atomic weight, 263. The emanation from radium has been condensed to a liquid; its vapour pressures have been determined in a modified Andrew's apparatus, and the volume of the liquid has also been measured. The boiling point under atmospheric pressure is $-62°$; the critical temperature is 104·5°, and the critical pressure is 47,450 mm. If these numbers are mapped on segments of circles on which the corresponding constants for argon, krypton,

and xenon lie, they intersect the ordinate of atomic weights at the figure 176. That appears to decide the atomic weight of the emanation; for if it be assumed as 219, the form of the curve would have to be completely altered, and, indeed, would become reflex. From another standpoint, the boiling point, with atomic weight 219, would be 49 degrees higher, and the critical point 53 degrees higher, than the points where the atomic weight ordinates cut these curves.

Discussion.

Sir William Ramsay added the following particulars to Dr. Gray's description of the results of their experiments: The volume of the emanation, calculated for 0° and 760 mm. pressure, is 0·6 cub. mm. per gram of radium in radioactive equilibrium; this confirms Rutherford's measurements. The sudden diminution of the volume of the emanation, remarked by himself and Soddy, again with Cameron, and by Rutherford, is due in all probability to the absorption of the foreign gas by the walls of the containing vessel under the influence of the emanation. It has been observed, too, that emanation also enters the walls of the tube. In Mr. Usher's experiments with ammonia, hydrogen disappeared, and was subsequently recovered from the broken-up tube by heating it in a vacuum.

***141. "Isolation and synthesis of *p*-hydroxyphenylethylamine, an active principle of ergot soluble in water." By George Barger.**

The isolation of *p*-hydroxyphenylethylamine,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,$$

from aqueous ergot extracts, and the synthesis of this physiologically active principle by the reduction of *p*-hydroxyphenylacetonitrile, were described.

***142. "Nitrotetramethyldiphenyl." (Preliminary note.) By Arthur William Crossley and Charles Herbert Hampshire.**

When fuming nitric acid is gradually added to *o*-xylene, there are obtained unchanged *o*-xylene, mononitro-*o*-xylenes, and a *nitrotetramethyldiphenyl*, $C_{16}H_{17}O_2N$ (*Trans.*, 1909, **95**, 217), crystallising from alcohol in clusters of stout, yellow, flattened needles, melting at 115°.

That the two benzene nuclei in this substance are linked together by carbon atoms of the nuclei and not by those of the methyl groups is proved by oxidation with dilute nitric acid, when a *nitrotetracarb-*

oxylic acid, $C_{12}H_5O_2N(CO_2H)_4$, is produced. It crystallises from water with $1H_2O$ in small, white clusters of hair-like needles, melting and evolving gas at 225°. The *tetraethyl* ester, $C_{12}H_5O_2N(CO_2Et)_4$, crystallises from alcohol in almost colourless, transparent, irregular needles, melting at 126—127°.

Nitrotetramethyldiphenyl is reduced by tin and hydrochloric acid to *aminotetramethyldiphenyl*, which separates from light petroleum in radiating clusters of transparent needles, melting at 81°.

Experiments are now in progress with the object of definitely establishing the exact positions of the various groups in this nitrotetramethyldiphenyl.

143. "Ammonium perhalides." By Frederick Daniel Chattaway.

The author has recently (*Proc.*, 1908, **24**, 172) expressed the view that the diazonium trihalides are *N*-trihalogen derivatives of the hydrazines. In order to compare their properties with those of the ammonium perhalides, the latter have been prepared and their behaviours studied. Only ammonium perbromide, ammonium periodide, and ammonium dibromoiodide have apparently been previously isolated. The supposed risk of explosion from liberation of nitrogen chloride appears to have hindered attempts to prepare the perhalides containing chlorine. Two of these compounds have now been prepared, and prove to be remarkably stable substances. *Ammonium dichloroiodide*, $NH_4 \cdot Cl_2I$, crystallises in large, brilliant scarlet prisms, and *ammonium chlorobromoiodide*, $NH_4 \cdot ClBrI$, in large, brilliant garnet-red prisms. Both can be kept in closed vessels for a long period without apparent change. When heated they do not explode, but lose two atoms of halogen, pure ammonium chloride being left. Both are extremely soluble in water, and deliquesce in damp air.

A study of the properties of the ammonium perhalides shows that they and the diazonium perhalides cannot be regarded as analogously constituted. For example, diazobenzene perbromide is a solid insoluble in water which can be preserved in a vacuum over lime for a long period with very slight loss in weight. Ammonium perbromide, on the other hand, is extraordinarily easily soluble in water, and loses two-thirds of its bromine if exposed for a few minutes in the air.

A large number of perhalides of primary amines have been prepared; these closely resemble the ammonium perhalides in properties.

144. "Studies in asymmetric synthesis. Part VIII. The asymmetric synthesis of *l*-mandelic acid." By Alex. McKenzie and Herbert Brooke Perren Humphries.

The authors described the asymmetric synthesis of *l*-mandelic acid. *l*-Menthyl benzoylformate was reduced by aluminium amalgam, the reduction product acetylated, and a lævorotatory mandelic acid mixture obtained by hydrolysis of the reduction product and subsequent complete elimination of the active menthol.

The isomeric *l*-menthyl acetylmandelates have also been investigated.

145. "Note on the condensation of acetone and hippuric acid." By William Henry Perkin, jun., and John Lionel Simonsen.

Hippuric acid and acetone readily condense in the presence of acetic anhydride and sodium acetate with formation of the *anhydride* of *α-benzoylamino-β-dimethylacrylic acid*, $CMe_2{:}C<^{N=CPh}_{CO\cdot O}$, which crystallises from dilute alcohol in almost colourless needles, m. p. 98—99°. When hydrolysed with alkalis or cold hydrochloric acid, it is converted into *α-benzoylamino-β-dimethylacrylic acid*, $CMe_2{:}C(NH\cdot COPh)\cdot CO_2H$, which separates from ethyl acetate in glistening needles decomposing at 217°. This acid, when heated with concentrated hydrochloric acid, is decomposed into benzoic acid and *dimethylpyruvic acid*,

$$CHMe_2\cdot CO\cdot CO_2H.$$

Dimethylpyruvic acid, which has not previously been obtained in a pure state, solidifies, when cooled, to thin leaflets melting at about 16°, and boils at 133—135°/200 mm. It yields an *oxime* decomposing at 161°, a *semicarbazone* decomposing at 176°, and a *hydrazone* decomposing at 152° (not 129° as stated by Brunner, *Monatsh.*, 1895, **15**, 763). Its *ethyl* ester boils at 173°/764 mm.

The authors wish to reserve this acid for further investigation.

146. "The physical properties of aqueous sodium sulphite." By Harold Hartley and William Henry Barrett.

In a systematic examination of the system sodium sulphite–water, the solubility of the two stable forms $Na_2SO_3,7H_2O$ and Na_2SO_3 has been determined, and a transition temperature has been found in the neighbourhood of 22°. The conditions under which either the hydrated modification or ice separates from a supersaturated solu-

tion have been studied; the extent of the metastable region in the former case amounts to as much as 30°. The crystallographic properties of the anhydrous salt have also been examined.

147. "**The preparation of disulphides. Part V. Diethyl esters of α-dithiodibutyric, α-dithiodi*iso*butyric, and α-dithiodi*iso*valeric acids.**" **By Thomas Slater Price and Douglas Frank Twiss.**

In continuation of previous work the *diethyl* esters of *α-dithiodibutyric, α-dithiodiisobutyric* and *α-dithiodiisovaleric acids* have been prepared by the electrolytic reduction of the mixtures obtained by the interaction of sodium thiosulphate with ethyl α-bromobutyrate, ethyl α-bromo*iso*butyrate, and ethyl α-bromo*iso*valerate respectively. These esters are all liquids heavier than water and distil unchanged under diminished pressure; the boiling points are as follows: diethyl α-dithiodibutyrate, 187°/22 mm.; diethyl α-dithiodi*iso*butyrate, 166°/19 mm.; diethyl α-dithiodi*iso*valerate, 173°/12 mm.

From these esters only *α-dithiodiisobutyric* acid could be prepared in a pure state; it is a solid, melting at 197—198°.

148. "**Relation between chemical constitution and physiological action in the tropeines. Part II.**" **By Hooper Albert Dickinson Jowett and Frank Lee Pyman.**

In continuation of former work on the subject, the authors have prepared and submitted to physiological examination a large number of tropeines, many of which had not been previously described. The physiological results indicated that the so-called Ladenburg's generalisation (which is not due to Ladenburg) cannot be strictly applied.

149. "**The formation of silicates, glasses, and glazes.**" **By John W. Cobb.**

On the assumption that a glass can be regarded as formed by the combination and solution of its constituent oxides, the author has studied the process of formation of the glass represented by the formula $Na_2O,CaO,Al_2O_3,10SiO_2$.

An investigation on the combination of lime and silica shows that the compounds formed are $2CaO,SiO_2$ and CaO,SiO_2.

Lime and alumina interact to form the compounds CaO,Al_2O_3,

$CaO,2Al_2O_3$, and an insoluble calcium aluminate, presumably containing a large amount of alumina.

The general question of chemical interaction between solids was discussed, and the conclusion was drawn that: (1) the temperature of formation of a slag and its fusion point are not identical, nor are they apparently related (in opposition to Boudouard's generalisation); (2) interaction between solids may go far, even to completion, without fusion; (3) from 800° upwards the state of mixed solid particles is one of fairly effective molecular contact, allowing free play to selective chemical affinities.

150. "The determination of the rate of decomposition of benzenediazonium chloride." By Francis Edward Everard Lamplough.

Some further experiments* have been made on the decomposition of benzene diazonium chloride, and direct measurements of the amount of nitrogen stored up in the solution have been obtained. When rather more than ordinary care is taken to keep the vessels and solutions free from dust and impurities, degrees of supersaturation up to 300 times the normal amount of gas dissolved have been observed.

Further experiments with direct measurement of temperature have confirmed the values of the constants previously obtained for the reaction (*Trans. Camb. Phil. Soc.*, 1908, **14**, 590).

151. "Acids as accelerators in acetylation." Part II. By Alice Emily Smith and Kennedy Joseph Previté Orton.

The speed of acetylation of *s*-tribromophenol in the presence of sulphuric, perchloric, and orthophosphoric acids has been measured. Whereas in acetic acid and chloroform solution, acetic anhydride has no perceptible action on *s*-tribromophenol at the ordinary temperature, even after keeping for several weeks, in the presence of perchloric and sulphuric acids, acetylation takes place very rapidly. Orthophosphoric acid (or phosphoric oxide) comes far behind as an accelerator. When the quantity of acid is small, the rate of the reaction is approximately proportional to its concentration. Comparing gram-molecular proportions, perchloric acid is about 2·5 times as effective as sulphuric acid.

Chloroform is the medium in which acetylation is the most rapid, but acetic acid is only slightly inferior. Benzene and acetone are unfavourable to acetylation.

* Compare *Trans. Camb. Phil. Soc.*, 1908, **14**, 580; *Proc.*, 1909, **25**, 24.

A comparison of pyridine, acids, and sodium acetate as accelerators of acetylation by acetic anhydride, shows that both the two former are far superior. Pyridine is approximately as effective as perchloric acid and therefore superior to sulphuric acid.

152. "Resolution of racemic alcohols." (Preliminary note.) By Robert Howson Pickard and Joseph Kenyon.

Pickard and Littlebury have recently described (*Trans.*, 1907, **91**, 1973) a method for the complete resolution of racemic alcohols by the fractional crystallisation of salts formed by acid esters of the alcohol with optically active bases. By this method they obtained the pure borneols and *iso*borneols, and have synthesised *l*-menthol from thymol (*Proc.*, 1908, **24**, 217).

The present authors in a similar way (*Trans.*, 1907, **91**, 2058) carried out the first successful resolution of an aliphatic alcohol, namely, that of octane-2-ol with $[\alpha]_D^{17} \pm 9{\cdot}9°$, and in view of work recently published abroad, wish to state that in conjunction with several collaborators they are engaged in applying the method to alcohols of very varied types.

Among the secondary alcohols already resolved (the specific rotatory power, $[\alpha]_D^{17}$, being given in brackets) are: butane-2-ol ($+13{\cdot}3°$); pentane-2-ol ($+14{\cdot}3°$); hexane-2-ol ($+11{\cdot}6°$); nonane-3-ol ($\pm 8{\cdot}0°$); phenylmethylcarbinol, ($+32{\cdot}8°$), and phenylethylcarbinol ($\pm 27{\cdot}3°$).

153. "Syntheses with phenol derivatives containing a mobile nitro-group. Part II. The interaction of 2:3:5-trinitro-4-acetyl-aminophenol and amines" (continued). By Raphael Meldola and James Gordon Hay.

In continuation of former researches (*Trans.*, 1906, **89**, 1935; 1908, **93**, 1659) the authors have studied the formation of iminazoles and other compounds quantitatively from the point of view of steric hindrance. The protective influence of substituents in the ortho-position is brought out very clearly in the recorded results. With the hydroxyl or methoxy-group in the para-position, some protecting influence is also exerted, the yields in the case of *p*-aminophenol and *p*-anisidine being less than with the corresponding meta-compounds. The general results obtained with the six series of isomeric substituted amines, namely, the chloroanilines, bromoanilines, nitroanilines, aminophenols, anisidines, and aminobenzoic acids, have been classified in the order of yield and compared with the results obtained by

Wedekind with picryl chloride. Experiments with the trinitro-compound and secondary amines have revealed the remarkable fact that catenation takes place only with dimethylamine and piperidine. All the homologues of dimethylamine, from diethylamine to di*iso*-amylamine, are without action. This fact has led the authors to suggest an extension of the hypothesis of steric hindrance to cases in which a mobile atom or radicle is protected on both sides by ortho-substituents, and in which the actual size of the radicles carried by the reacting compound determines the possibility of catenation.

All the new iminazoles and *m*-aminophenol derivatives prepared in the course of the research were described and characterised.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, June 7th, 1909.

All persons who received grants in June, 1908, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Tuesday, June 1st.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

At the next Ordinary Meeting on **Thursday**, June **3rd**, 1909, at **8.30** p.m., Professor Frank Wigglesworth Clarke will deliver the Wolcott Gibbs Memorial Lecture, and the following papers will be communicated :

"The molecular weight of tetraethylammonium bromide and the atomic weight of carbon." By A. Scott.

"The rate of formation of azo-derivatives from benzenoid diamines." By V. H. Veley.

"The synthesis of substances allied to cotarnine." By A. H. Salway.

"Monomethylfructose and its derivatives. Constitution of fructose-diacetone." By J. C. Irvine and A. Hynd.

"On optically active δ-oximino-hexahydrobenzoic acid and the configuration of the oximino-group." (Preliminary note.) By W. H. Mills and Miss A. M. Bain.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 358.

Thursday, June 3rd, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs.:

Hardee Chambliss, Ph.D., 56, W. 36th Street, New York City, U.S.A.

Edward Walter Taplin, Church House, Heavitree, Exeter.

A certificate has been authorised by the Council for presentation to ballot under Bye-Law I, par. 3, in favour of Dr. Hassum A. Lakhani, Murud Janjira, India.

Professor FRANK WIGGLESWORTH CLARKE, of Washington, then delivered the Wolcott Gibbs Memorial Lecture, at the conclusion of which Professor Sir JAMES DEWAR moved a vote of thanks to Professor Clarke.

Professor THORPE, in seconding the motion, congratulated the Society in securing in their Honorary Foreign Member, Prof. Clarke, one so eminently capable of doing justice to the signal services which his deceased countryman, the late Dr. Wolcott Gibbs, had rendered to chemical science. The Chemical Society justly prided itself on the distinction conferred upon it by the distinguished men who constituted the class of its Honorary Members. They honoured them living, and when death summoned them from the scene of their activities, they sought to honour them dead, and by lectures such as they had heard

to-night to commemorate their achievements and to indicate their relation and true position towards the science which they had laboured to advance. In putting together the story of Dr. Wolcott Gibbs' life and work, Dr. Clarke had enjoyed the advantage of contact and intimate personal acquaintance with his subject, and it was this personal note which rendered his discourse specially interesting and valuable.

Professor Otto N. Witt expressed his great satisfaction at having been able to listen to Professor Clarke's lecture, which not only deserved the greatest praise for its literary and scientific merits, but had also a great personal interest for himself.

In the German Chemical Society it was customary for the death of prominent members to be announced by the president in the meeting following the sad event, and a short biographical sketch had to be given on such occasions, pending the publication of an elaborate essay at the end of the year. Thus it had been his (the speaker's) duty to give an account of the life and labours of Wolcott Gibbs in one of the meetings of the Society. In compiling the necessary notes, he had observed how scant the existing information was, and the short time at his disposal had not allowed him to ask Professor Clarke for a few notes as he would like to have done. There were a few things, however, which made it quite certain that Gibbs, who was an honorary member of the German Chemical Society as well as of the English one, had been deserving of the greatest esteem. It was quite evident that he had enjoyed the sincere friendship of the great founder of the German Society, A. W. Hofmann, whose name was also a household word amongst English chemists. And it was equally certain that Gibbs possessed great merits as a teacher and as the head of the brilliant and successful school of American chemists, of which Professor Clarke, whom the speaker had learned to know and to admire during his stay in the United States, was the most distinguished representative. Whilst supporting the motion for a vote of thanks to Professor Clarke, he begged to thank the President for having given him this opportunity for paying a tribute of personal admiration both to the memory of Wolcott Gibbs and to Professor Clarke, who had pictured the life and the work of his dead master in words that had come from the depth of his heart.

Professor Charles Baskerville said that the honour paid him by the President in asking him to support the vote of thanks proposed by Sir James Dewar was, he knew, intended as a personal one. He was endeavouring to fill the Chair, the third in line, first occupied by the distinguished lamented subject of Dr. Clarke's eloquent eulogy. He wished, however, to emphasise something more significant. As mentioned by the lecturer, Wolcott Gibbs was the founder of the

Union League Club of New York, which organisation sought to preserve the Union. His (the speaker's) father and all his relations sought to dismember that Union for reasons they thought good. The Union was happily preserved, however, and a scion of the Confederate States was now carrying forward the educational work inaugurated by the deceased patriot. Chemistry thus showed itself in a social way as the crucible of civilisation.

It gave him peculiar personal pleasure to support the motion for another reason unknown to many of those present. Professor Clarke was his chemical grandfather, for he taught Professor Dudley, who was also present, and who in turn had taught him (the speaker). His pride in the delightfully charming manner in which Dr. Clarke, the pupil, had shown his appreciation of his former master could therefore well be understood.

The PRESIDENT said that, in its Memorial Lectures, he thought the Chemical Society had learnt to look for three excellences.

They wished in the first place to have recorded the main steps in the career of the distinguished chemist whom they were met to commemorate, so that they might appreciate the difficulties he faced and how he surmounted them—difficulties which could only be made real to them by one who was a past master of their science; secondly, they looked for some personal and sympathetic touches to tell a younger generation what kind of man was he who was gone; and lastly, they were delighted when the story was told them, not only scientifically and sympathetically—but with that arrangement and perspective and charm of language which could turn even chemistry into literature.

They could congratulate themselves that in all these excellences the lecture of Prof. Clarke fulfilled, and more than fulfilled, their ideals.

The vote of thanks was put to the meeting, carried by acclamation, and acknowledged by Professor CLARKE.

Of the following papers, those marked * were read:

*154. **"The molecular weight of tetraethylammonium bromide and the atomic weight of carbon." By Alexander Scott.**

The author gave an account of his endeavours to determine the molecular weight of a hydrocarbon with a degree of accuracy comparable to that attained in the determination of the atomic weights of many elements. This has been done for C_8H_{16} by titrating pure tetraethylammonium bromide against pure silver, after the manner of Stas. To precipitate 107·93 parts of silver, 210·324 parts of

$N(C_2H_5)_4Br$ were required, whilst for the same weight of silver 97·995 parts of ammonium bromide were necessary. Subtracting

from	210·324	= $NC_8H_{20}Br$
	97·995	= $N\ H_4\ Br$.
we obtain	112·329	= C_8H_{16}

If we take H = 1·0075, then H_{16} = 16·12, which gives 112·329 − 16·120 = 96·209 = C_8 or C = 12·026.

This number has been corroborated by a titration made in the same way of a small quantity of tetramethylammonium bromide, which gave 154·150 = $N(CH_3)_4Br$, and, similarly, 56·155 for C_4H_8 and C = 12·024. Taking 107·88 as the atomic weight of silver, we get C = 12·018.

Discussion.

Professor F. W. Clarke called attention to the fact that the new value proposed for the atomic weight of carbon was notably higher than that found by recent investigators with physical methods. From the densities of carbon dioxide, carbon monoxide, and methane, the atomic weight of carbon was very near 12. In Lenher's determinations of the atomic weight of tellurium, a value had just been found of 127·33, calculated with the international figures for silver, potassium, chlorine, and bromine of several years ago. This result was lower than the best results obtained by others. But on recalculating Lenher's work with the new value for the other atomic weights, the value for tellurium was 127·55, in close agreement with former determinations. Hence, the discrepancy was due, not to the work done, but to the antecedent factors used in calculation. How far the discordance in the figures for carbon might be due to similar causes it was too soon to say, but part of it was thus to be explained.

Sir W. Ramsay called attention to the possibility of included mother liquor in the ammonium bromide and the tetraethylammonium bromide.

In reply, Dr. Scott pointed out that the methods employed in precipitating and drying the various specimens of the salt, as well as the very close agreement of the results, seemed to exclude all probability of the dried salt containing any mother liquor. The atomic weight taken for silver (107·93) rendered the results more readily comparable with those of Stas, whilst the value 107·88 at present adopted by the International Committee, as Dr. Thorpe had pointed out, was probably only of transient interest and might, by further research, be still further lowered.

155. "The rate of formation of azo-derivatives from benzenoid diamines." By Victor Herbert Veley.

It was shown that (i) the rate of formation, as studied by a tintometer method, of azo-compounds from benzenoid diamine hydrochlorides and sodium nitrite is conditioned by the hydrochloric acid and monohydrochloride liberated by hydrolysis. It is an example of a simultaneous linear reaction expressed simply as $\Delta x/\Delta t = k$.

(ii) The total amount of dyestuff capable of being formed, or range, is a linear function of concentration, but the increase of rate is a logarithmic function of the concentration expressed as $\log k_n = \log k_1 + a \log c$ (c = concentration, a = constant to be evaluated from the results).

(iii) The rate is a logarithmic function of absolute temperature according to the expression $k_1/k = (T_1/T)^m$.

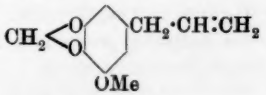
(iv) The addition of hydrochloric and other acids produces an initial acceleration, but a total retardation, the reaction sooner coming to an end, and consequently the amount of dyestuff capable of being formed is thereby diminished.

(v) The substitution of hydrogen by the methyl grouping (comparison of phenylene- and tolylene-diamine—Bismarck Brown and Vesuvine) causes a slight decrease in rate, but a considerable decrease in the total amount of dyestuff capable of being formed.

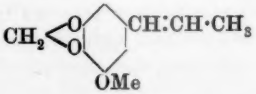
It is considered probable that this is a result of the more ready decomposition of the intermediate diazo-compound in the case of the latter than in that of the former.

156. "The synthesis of substances allied to cotarnine." By Arthur Henry Salway.

The material employed as the starting point in this investigation was myristicin (3-methoxy-4 : 5-methylenedioxy-1-allylbenzene), which was obtained from the essential oil of nutmeg (compare Power and Salway, *Trans.*, 1907, **91**, 2037). The successive stages in the synthesis are represented by the following compounds : (I) myristicin, (II) *iso*myristicin, (III) myristicinaldehyde, (IV) nitromyristicinaldehyde, (V) nitromethoxymethylenedioxycinnamic acid, (VI) ketomethoxymethylenedioxydihydroquinoline, (VII) ketomethoxymethylenedioxymethyldihydroquinoline, and (VIII) oxy*iso*cotarnine.



(I.)



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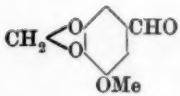
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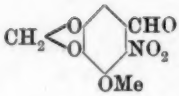
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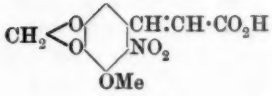
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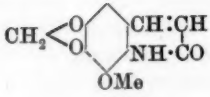
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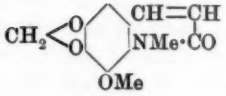
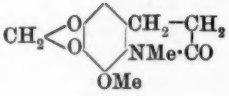

(VII.)


(VIII.)

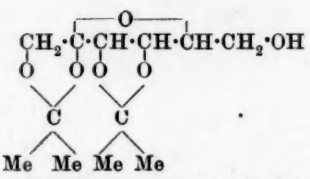
Ketomethoxymethylenedioxydihydroquinoline, ketomethoxymethylenedioxymethyldihydroquinoline, and oxy*iso*cotarnine are closely related to cotarnine, and their physiological action is at present under investigation.

An account was also given of several attempts to synthesise cotarnine, which, however, were unsuccessful.

157. "Monomethyl lævulose and its derivatives. Constitution of lævulosediacetone." By James Colquhoun Irvine and Alexander Hynd.

Lævulosediacetone yields on methylation by the silver oxide reaction a crystalline derivative (*monomethyl α-laevulosediacetone*), melting at 115°, and having $[\alpha]_D^{20}$ −136·4° in methyl-alcoholic solution. The compound is very easily hydrolysed by dilute acids to give *monomethyl laevulose*, which is apparently the first definite example of a mono-substituted sugar other than the glucosides or the metallic derivatives. The sugar crystallises from ethyl acetate in the pure α-form, which displays mutarotation in the downward sense: $[\alpha]_D^{20}$ −70·5° ⟶ −53·1°. On the other hand, fusion gives an excess of the β-form, and the reverse optical change ensues on solution. The compound yielded *monomethylglucosazone* as yellow needles, melting at 142°, and was oxidised by bromine water to *αβ-dihydroxy-γ-methoxybutyric acid*.

These results show that the methyl group in the alkylated ketose is in the δ-position with reference to the reducing group, and, according to this view, the structure of lævulosediacetone must be



In addition, it has been shown that the alkylated sugar condenses readily with acetone or with methyl alcohol, and the products thus obtained are interconvertible under suitable conditions. The specific rotations of the various compounds described show that the total optical effect resulting from complete methylation of the sugar molecule is the additive sum of oppositely directed values.

158. "**Optically active 4-oximino*cyclo*hexanecarboxylic acid and the configuration of the oximino-group.**" (Preliminary note.) **By William Hobson Mills and Alice Mary Bain.**

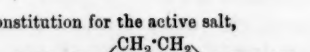
When a sufficiently dilute solution of equimolecular proportions of 4-oximino*cyclo*hexanecarboxylic acid (W. H. Perkin, *Trans.*, 1904, **85**, 427) (4·7 grams) and quinine (9·7 grams) in ethyl acetate is allowed to evaporate slowly at the ordinary temperature, a quinine salt crystallises in silky needles during the course of two or three days.

The salt thus obtained was recrystallised three times from ethyl acetate and then decomposed by suspending it in water, carefully adding a slight excess of dilute aqueous sodium hydroxide, and extracting repeatedly with ether to remove quinine. There was thus obtained a slightly alkaline solution of sodium salt, from which all quinine had been removed, corresponding with about 1·8 grams of oximino-acid. On polarimetric examination in a 2-dcm. tube, very distinct lævorotation was observed, namely, $\alpha_D^1 -4{\cdot}4°$. The optical activity was immediately destroyed by acidification with dilute hydrochloric acid.

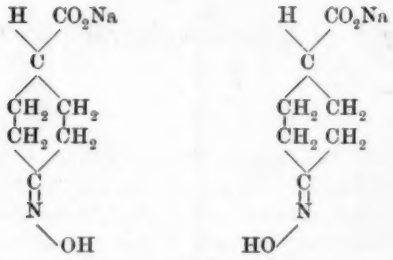
From the above observations, it appears probable that the sodium salt of 4-oximino*cyclo*hexanecarboxylic acid can exist in a dextro- and lævo-modification, as well as the inactive form corresponding with the acid described by Perkin.

Since in a compound of this constitution enantiomorphism is possible only if the three valencies of the nitrogen atom of the oximino-group do not lie in one plane, the two active forms must correspond with the two configurations* :

* An alternative constitution for the active salt,



is very improbable, since acidification, which would be expected to favour the grouping :C·NH·OH relatively to C:NOH, at once destroys the activity.



The existence of an optically active form of this substance thus affords evidence of the validity of the fundamental hypothesis in the Hantzsch-Werner theory of the isomerism of the oximes. It is also of interest in connexion with the recent work on optically active substances which do not contain an asymmetric carbon atom in the narrower sense (Perkin and Pope, *Trans.*, 1908, **93**, 1075; Harding, Haworth, and Perkin, *ibid.*, 1943; Perkin, Pope, and Wallach, *Proc.*, 1909, **26**, 83; also Marckwald and Meth, *Ber.*, 1906, **39**, 1171, etc.).

The authors are proceeding with this investigation, and hope in due course to submit a complete account of their results.

159. "*cyclo*Butane-1 : 3-dicarboxylic acid and some of its derivatives." By William Henry Perkin, jun., and John Lionel Simonsen.

The authors described the action of hydrobromic acid and of bromine on *cyclo*butane-1 : 3-dicarboxylic acid and on norpinic acid, and discussed the conditions under which disruption of the *cyclo*butane ring takes place in these and analogous cases.

160. "The oxidation of mucic acid in presence of iron." By Frederic Ferraboschi.

The oxidation of mucic acid by means of hydrogen dioxide in presence of iron has been investigated. The principal product is a strongly reducing acid, which appears to be a *dihydroxymucic acid*. It may also be regarded as a diketonic acid, namely, *dihydroxydiketoadipic acid*. Its *dihydrazone* has been prepared.

Parallel experiments on the oxidation of saccharic acid gave analogous results, but the products obtained are not identical with those derived from mucic acid.

161. "The production of ozone in the interaction between hydrogen dioxide and sulphur dioxide." (Preliminary note.) By Frederic Ferraboschi.

In an investigation of the well-known reaction between sulphur dioxide and hydrogen dioxide, it has been observed that ozone is produced in considerable quantities.

It is found that when sulphur dioxide is rapidly led into a solution of hydrogen dioxide (both "10 volume" and "20 volume" strengths were used), it is entirely destroyed in passing through a layer 2 or 3 cm. deep. Each bubble almost, but not entirely, disappears, and ozone is produced in quantities sufficient to be easily detected by its odour. Its presence may be further proved by its actions on starch-potassium-iodide paper, and on paper moistened with an acetic acid solution of *pp'*-tetramethyldiaminodiphenylmethane ("tetra-base").

The production of ozone can also be observed when excess of hydrogen dioxide is added to aqueous sulphurous acid.

The same effect is not produced in the reaction of hydrogen dioxide with sodium sulphite or thiosulphate, or when sodium or barium peroxides, either with or without an acid, are added to aqueous sulphurous acid.

The reaction is being examined quantitatively.

162. "The action of sulphur monochloride on salts of organic acids: a convenient method of preparing anhydrides." By William Smith Denham.

When sodium benzoate is boiled with a solution of sulphur monochloride in light petroleum, a compound of the probable formula $(C_6H_5 \cdot CO_2S)_2$ is formed, which is very unstable and soon decomposes, giving sulphur, sulphur dioxide, and benzoic anhydride. The formation of this compound takes place more easily if the silver salt is used. Similar derivatives of acetic, propionic, phenylacetic, and the toluic acids have been obtained.

The easy formation and simple decomposition of these compounds suggests a method of preparing the anhydrides of the acids.

Sulphur monochloride reacts also with metallic derivatives of imides.

163. "The velocity of decomposition of nitroglycerin by heat." Part I. By Robert Robertson.

Nitroglycerin (glyceryl trinitrate) is heated in a current of carbon dioxide in an apparatus arranged to condense any volatilised nitro-

glycerin and, on rotation about an oblique axis, return it to be again heated. The nitrogen peroxide evolved is determined by Robertson and Napper's spectroscopic method (*Trans.*, 1907, **91**, 761). The products of decomposition are then passed over red-hot copper and copper oxide, and the nitrogen is measured over potassium hydroxide. It was found that nitroglycerin decomposes uniformly, yielding nitrogen peroxide, that the rate of decomposition is a function of the temperature, being doubled for every 5° between 95° and 125°, and that the rate of decomposition is higher than that of guncotton.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Baron, *Harold.* Chemical industry on the Continent. A report to the Electors of the Gartside Scholarships. pp. xi + 71. Manchester 1909. (*Recd.* 20/5/09.)

From the Publishers: Messrs. Sherratt & Hughes.

International Congress of Applied Chemistry, VII. *Explosives Section.* The rise and progress of the British explosives industry. pp. xiv + 418. ill. London 1909. (*Recd.* 25/5/09.)

From the Publishers: Messrs. Whittaker & Co.

Matthews, *J. Merritt.* Laboratory manual of dyeing and textile chemistry. pp. xii + 363. New York 1909. (*Recd.* 19/5/09.)

From the Publishers: Messrs. John Wiley & Sons.

Schimpf, *Henry W.* A manual of volumetric analysis for the use of pharmacists, sanitary and food chemists. 5th edition. pp. xx + 725. ill. New York 1909. (*Recd.* 19/5/09.)

From the Publishers: Messrs. John Wiley & Sons.

Stone, *C. H.* Practical testing of gas and gas meters. pp. x + 337. ill. New York 1909. (*Recd.* 19/5/09.)

From the Publishers: Messrs. John Wiley & Sons.

Zsigmondy, *Richard.* Colloids and the ultramicroscope. Authorized translations by *Jerome* **Alexander.** pp. xiii + 245. ill. New York 1909. (*Recd.* 19/5/09.)

From the Publishers: Messrs. John Wiley & Sons.

II. *By Purchase.*

Werner, *A.* Neuere Anschauungen auf dem Gebiete der anorganischen Chemie. pp. xv + 292. II Auflage. Braunschweig 1909. (*Recd.* 19/5/09.)

LIST OF FELLOWS, 1909.

The List of Fellows for 1909 is now in active preparation, and changes of address received after 31st July cannot be included in it.

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

At the next Ordinary Meeting on **Thursday**, June **17th**, 1909, at 8.30 p.m., there will be a ballot for the election of Fellows and the following papers will be communicated:

"The carbonate of copper and the cupricarbonates." By S. P. U. Pickering.

"*iso*Quinoline derivatives. Part I. Oxidation of laudanosine." By F. L. Pyman.

"The colour and constitution of azo-compounds." By J. T. Hewitt and W. Thomas.

"*iso*Iminazolone." By H. J. H. Fenton and W. A. R. Wilks.

"Homologues of furfural." By H. J. H. Fenton and F. Robinson.

"Studies of dynamic isomerism. Part IX. The relationship between absorption spectra and isomeric change. Absorption spectra of sulphonic derivatives of camphor." By T. M. Lowry and C. H. Desch.

"The relation between the strength of acids and bases and the quantitative distribution of affinity in the molecule." Part II. By B. Flürscheim.

"The oxidation of hydroxy-derivatives of benzaldehyde and acetophenone." By H. D. Dakin.

"The intramolecular rearrangement of diphenylamine orthosulphoxides." By E. de B. Barnett and S. Smiles.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, June 17th, 1909.

Annett, Harold Edward,

Imperial Research Institute, Pusa, Behar, Bengal, India.

Supernumerary Agricultural Chemist, at present acting as Imperial Agricultural Chemist in the Indian Agricultural Service, Imperial Department. 1. B.Sc. (Agriculture) of London University. 2. A member by Diploma of the South-Eastern Agric. College (Lond. Univ.) with Honours in Agricultural Chemistry. 3. Demonstrator in Chemistry and Analyst at above College, 1906–7. 4. Acted as Agricultural Chemist to the Government of Bombay, and lectured in Chemistry in the Poona Agricultural College, Aug.–Nov., 1908. 5. Author with Dr. E. J. Russell of "Composition of Green Maize and the Silage produced therefrom," *Journal Agricultural Science*, 1908, Vol. 2.

J. Walter Leather. M. J. R. Dunstan.
Robert S. Finlow. A. D. Hall.
E. J. Russell.

Arnfield, Harold,

Peak Lodge, Buxton Road, Stockport.

Pharmaceutical Chemist.

Arthur W. Crossley. Chas. Horne Warner.
Charles Gilling. *M. O. Forster.*
Alexander Scott.

Dunlop, John Gunning Moore,

St. Helen's, Holywood, Belfast, and Caius College, Cambridge.

Undergraduate. Scholar of Caius College, Cambridge. Collaborated

with H. O. Jones in investigation of "Action of Ethylene Dibromide on Monomethyl Aniline" (*Trans.*, 1909, p. 416).

S. Ruhemann. H. J. H. Fenton.
H. O. Jones. W. J. Sell.

W. J. Pope.

Edge, John Harold,

Great Marld, Smithills, Bolton.

Technical Chemist. Works Chemist at Messrs. Wm. Edge & Sons, Ltd., Bolton. Studied Chemistry 4 years under Dr. Marshall, of Leighton Hall College; also at the Royal Technical Institute, Salford, and Manchester University. Anxious to keep in touch with the latest chemical research.

J. R. Appleyard. E. Clark.
B. Prentice. *J. Wertheimer.*

John S. Lumsden.

Egerton, Alfred Charles Glyn,

Chilton House, Thame, Oxfordshire.

Research student at present. B.Sc. (Chemistry Hons.), London, 1908. "Vapour Pressure of Bromine at Low Temperatures" (not yet published), and "Divergence of Atomic Weights from Whole Numbers" (*Trans.*, 1909, p. 238).

T. C. Porter. W. H. Gibson.
William Ramsay. R. W. Gray.

S. Smiles.

Essex, jun., Harry,

23, Bescot St., Walsall.

Blast-Furnace Chemist. Chief Chemist to Messrs. G. & R. Thomas, Bloxwich and Walsall; teacher of Practical and Theor. Metallurgy at Municipal Institute, Walsall; King's Prize, Stage III, Theor. Metallurgy, and Bronze and Silver Medals in Iron and Steel Manufacture, City and Guilds Institute. Certificates in Stages II and III Chemistry, B. of E.

Arthur Adams. Harry Silvester.
Frank E. Thompson. *J. B. Coleman.*

Wm. Oldershaw.

Hibbert, Harold,

"Creston," Marple Bridge, Derbyshire.

Research Chemist. Master of Science (Vict.); Ph.D. (Leipzig); F.I.C. Author or joint author of some twelve original publications dealing with organic chemistry, published in the *Transactions of the*

Chemical Soc., Berichte der Deutsch. Chem. Gesellschaft, and Liebig's *Annalen.*

Harold B. Dixon. Jocelyn F. Thorpe.
Wm. A. Bone. G. H. Bailey.
W. H. Perkin.

Kirby, Oswald Farquhar,
14, Wellclose Mount, Leeds.

Lecturer on Chemistry. Master of Arts (First Class Honours in Mental Science), Aberdeen University; Bachelor of Science (1st in Honours Class of Organic Chemistry, and 1st prizeman in Agricultural Chemistry, Theoretical and Practical), Aberdeen; Head of the Chemical Department, Modern School, Leeds; Lecturer in Organic Chemistry, Technical School, Leeds.

F. R. Japp. A. N. Meldrum.
James Hendrick. James C. Philip.
T. S. Murray. *F. W. Branson.*

Matchet, Andrew Sneddon,
13, Bute Gardens, Cathcart.

Analytical Chemist. Chief Chemist, Scottish Wholesale Co-operative Society, Ltd., Shieldhall, Govan. Student with Messrs. R. R. Tatlock, City Analysts, Glasgow, for over 2 years.

R. R. Tatlock. Harry Dunlop.
R. T. Thomson. William S. Denham.
Thomas Gray.

May, Roland Josiah,
Granaugh Villa, Dunbar, Scotland.

Analytical Chemist to The British Malt Products Co., of London, Accrington, and Dunbar. Six years' tuition in Chemistry at the Central Foundation Schools of London. Student at the Northern Polytechnic and the Hackney Institute; 3 years Assistant to Leo. Taylor, F.I.C., Public Analyst for Hackney.

Edwin C. Jee. *Thomas H. Pope.*
Edwin M. Eagles. *L. T. Thorne.*
E. Geo. Streimer. *E. Haynes Jeffers.*

Napier, Thomas,
Arbiene, Clarkston, Busby.

Analytical Chemist. Studied at the Glasgow Technical College, and have been employed by the Cassel Cyanide Co., Ltd., for eleven years.

Thos. Ewan. G. G. Henderson.
J. H. Young. Thomas Gray.
William S. Denham.

Picton, **Norman**,

4, Pembroke Square, Kensington, W.

Works Chemist. Ph.D. (Leipzig), B.Sc. (Wales); 1851 Exhibition Scholar, 1906–08. Joint author of "Influence of Substituents in the Trinitrobenzene Molecule on the Formation of Additive Compounds with Arylamines" (*Trans. Chem. Soc.*, 1906).

Henry E. Roscoe. J. J. Sudborough.
P. Phillips Bedson. T. Campbell James.
J. W. Dodgson.

Resker, **Herbert Charles**,

The Sugar Works, Cossipore, Calcutta, India.

Chemist and Assistant of Cossipore Sugar Works. Late Science Scholar of Corpus Christi College, Cambridge. Cambridge Natural Science Tripos, Part I, Class I; Part 2, Class 2. Assistant Demonstrator in Chemistry at the Cambridge University Laboratory, 1905–1908.

W. J. Sell. H. O. Jones.
H. J. H. Fenton. J. E. Purvis.
F. W. Dootson.

Robinson, **Fred.**,

Broadway, Skerton, Lancaster.

Now engaged in research at Cambridge University Chemical Laboratories. First Class Natural Sciences Tripos, Part I, 1907; 2nd ditto, ditto, Part II, 1908 (Chemistry). Second Class Honours (Chemistry) London B.Sc., 1908. Late Scholar and Prizeman of Peterhouse Cambridge. Assistant Demonstrator in Univ. Chemical Laboratories, Cambridge, 1908–1909.

W. J. Sell. H. O. Jones.
H. J. H. Fenton. J. E. Purvis.
F. W. Dootson.

Sawbridge, **Barth. Frere**,

Thelnetham Rectory, Diss, Norfolk.

Chemical Analyst. 2nd Class Final Honour School of Natural Science (Chemistry), 1906; Associate Institute of Chemistry; Assistant to A. C. Chapman, Esq., F.I.C., F.C.S.; Assistant Demonstrator in Bacteriology at Battersea Polytechnic.

Alf. Chaston Chapman. W. W. Fisher.
F. Guy Stirling Baker. G. W. Monier-Williams.
Fredk. T. Harry.

Wills, Harry Sampson,

59, Caldecott Road, Denmark Hill, S.E.

Analytical Chemist. Formerly Chemist in the Laboratories of Burgoyne, Burbidges & Co.; subsequently Analyst with Messrs. Lorimer & Co., and now Analytical and Research Chemist with the firm of Boilerine, Limited.

Albert E. Bell.	T. W. Firth Clark.
Thos. Farries.	*T. Pitt.*
Reginald G. Halstead.	*F. W. Brown.*
T. G. Joyce.	*J. Brierley.*

Woods, George James,

2, Wellmeadow Road, Lewisham, S.E.

Schoolmaster. I have been a student of Chemistry since 1900, and am at present working in the Laboratory of the Goldsmiths' College. Although at present reading for an Honours degree in Chemistry, I intend at the earliest opportunity to proceed to research work in the subject, and to take up the science as a profession. I am desirous of securing privileges which attach to the Fellowship of the Society.

E. Wechsler.	W. H. Ratcliffe.
R. W. L. Clarke.	*A. T. Larter.*
Arthur Lapworth.	*M. White Stevens.*

H. Harding.

The following Certificate has been authorised for presentation to Ballot by the Council under Bye-law I (3):

Lakhani, Hassum A., M.D.,

Murud-Janjira (Bombay Presidency, India).

Chief Medical Officer, Janjira State (India). Doctor of Medicine of the University of Brussels. Chief Medical Officer and Health Officer and Chief Chemical Analytical Officer of Janjira State. Has special interest in Chemical researches. Has prepared the fragrant oils and essences from Indian fragrant flowers.

I. B. Lyon. *Albert Cooper.*

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 29/6/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 359.

Thursday, June 17th, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

Messrs. W. L. Dudley, A. H. Elliott, and G. B. Walker were formally elected Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Benjamin Leech, M.A., Beech Knoll, Macclesfield.
Frederic William Robinson, B.Sc., Grove House, Farnworth, Widnes.
Prof. Dr. Hermann Thoms, Berlin, Steglitz, Hohenzollernstr. 3.
Everard Cecil Van Essen, 28, Hereford Road, Snaresbrook, N.E.

A Certificate has been authorised by the Council for presentation to Ballot under Bye-law I, par. 3, in favour of A. K. Yegna Narayan Aiyer, M.A., Bangalore, India.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected:

Harold Edward Annett, B.Sc.
Harold Arnfield.
John Gunning Moore Dunlop.
John Harold Edge.
Alfred Charles Glyn Egerton, B.Sc.
Harry Essex, jun.
Harold Hibbert, M.Sc., Ph.D.
Oswald Farquhar Kirby, M.A., B.Sc.
Hassum A. Lakhani, M.D.
Andrew Sneddon Matchet.
Roland Josiah May.
Thomas Napier.
Norman Picton, B.Sc., Ph.D.
Herbert Charles Resker, B.A.
Fred. Robinson, B.A., B.Sc.
Barth. Frere Sawbridge, B.A.
Harry Sampson Wills.
George James Woods.

Of the following papers, those marked * were read:

***164. "The carbonates of copper and the cupricarbonates." By Spencer Umfreville Pickering.**

Besides the mineral azurite, $3CuO,2CO_2,H_2O$, and the ordinary carbonate of copper, malachite, $2CuO,CO_2,H_2O$, the following carbonates have been isolated.

$5CuO,2CO_2$: a blue, bulky precipitate, obtained by the precipitation of copper salts by sodium carbonate. $5CuO,3CO_2$: a light blue, stable precipitate, obtained by precipitation with sodium hydrogen carbonate. $8CuO,3CO,6H_2O$: a rather dark blue substance, obtained by the action of water on the double carbonate of copper and sodium.

All the basic carbonates are insoluble in water and in sodium carbonate solution, but they dissolve slightly in aqueous carbonic acid and in acid carbonates, a normal copper carbonate, or a double carbonate of copper and the alkali metal, being formed. The latter is obtained as a molecular compound in rather light blue crystals from such solutions, although in the solutions it is present in another form, as sodio-cupric carbonate, of the constitution: NaO·CO·OCuO·CO·NaO. In this compound the copper is electro-positive, but has a colour thirty times more intense than the copper in copper sulphate. When excess of sodium carbonate is added to it, the copper becomes electro-negative, and has a colour eighty times more intense than that in copper sulphate. The substance then present is an α-cupricarbonate, consisting of $Na_2Cu(CO_3)_2$ united with Na_2CO_3, but in which the copper is joined to the carbon atoms, and is in a quadrivalent condition. It oxidises dextrose, and the constitution suggested represents the presence of a loosely combined oxygen atom explaining such a reaction. Excess of sodium hydroxide decomposes it, but a greater excess dissolves the precipitated basic carbonate to form a deep violet-blue solution of the β-cupricarbonate, which consists of $Na_2Cu(CO_3)_2$ united with 1 or 2NaOH. This, too, oxidises dextrose, and also combines with cellulose. It is stable in presence of excess of alkali, whereas the α-compound gradually decomposes, either into the crystalline double salt or into malachite. The sodio-cupric carbonate decomposes in a similar manner.

Discussion.

Mr. W. C. Reynolds expressed the opinion that although it was possible to give to the double carbonates the structural formula which the author had done, they did not afford a satisfactory explanation, since certain of the double succinates (*Trans.*, 1898, **73**, 703), which were exactly analogous, and exhibited the same behaviour in solution, had the composition $K_4R(C_4H_4O_4)_3$, where R is Cu or Co. Such

compounds could not be formulated in the way described by the author, and it appeared probable that the constitution of the cupri-carbonate could be explained by molecular association with water of crystallisation, thus involving the idea of quadrivalent oxygen.

Mr. W. A. Davis suggested that in assigning structures to the mixed or double carbonates, the water of crystallisation probably ought to be considered; he had previously shown that the so-called trihydrate of magnesium carbonate, $MgCO_3,3H_2O$, was in reality a hydrated hydroxy-carbonate, $OH{\cdot}MgCO_3H,2H_2O$ (*J. Soc. Chem. Ind.*, 1906, **25**, 788), and had ascribed the impossibility of preparing normal copper carbonate by precipitation to the great tendency to the formation of mixed alkali copper carbonates, the hydrolysis of which gave rise to basic carbonates. In the case of magnesium he had succeeded in giving a proof that the very numerous "basic carbonates" were really mixtures of three compounds, $OH{\cdot}MgCO_3H$,

$$OH{\cdot}MgCO_3H,2H_2O,$$

and $Mg(OH)_2$, in varying proportions. In the case of copper there was slender evidence as to the existence of definite basic carbonates other than malachite and azurite.

Mr. E. H. Jeffers asked if Mr. Pickering considered the formula given for the α-cupricarbonate was analogous to Fehling's blue salt, because in the latter the copper had been shown to be in the electro-positive condition.

He was inclined to think that these compounds were simply molecular aggregates, in which the alkali hydroxide took the place of water of hydration. For instance, the corresponding citric acid compound was a peculiar peacock-green colour, easily reduced by sugar, but on addition of a little alkali hydroxide one obtained an intensely blue solution, exactly similar to Fehling's blue salt.

Moreover, more than one salt could be prepared from Fehling's solution, but on shaking the latter with alcohol, separating, and washing for hours with alcohol, the blue compound obtained was strongly alkaline.

Mr. Pickering said, in reply, that since the cupricarbonates could not be isolated, the formulæ given for them must be regarded only as suggestions. Very probably they were symmetrical, which, in the case of the α-compound, would involve the combination of $3Na_2CO_3$ with every $CuCO_3$, as suggested by Mr. Reynolds. The constitution of Fehling's solution had not been investigated, beyond ascertaining that its oxidising properties depended on the presence of electro-negative copper. The nature of the action between cellulose and the β-cupri-carbonate was not clear, but the former appeared to be unaffected by it after the copper was removed.

***165. "*iso*Quinoline derivatives. Part I. Oxidation of laudanosine." By Frank Lee Pyman.**

Just as narcotine and hydrastine yield on oxidation opianic acid together with cotarnine and hydrastinine respectively, so laudanosine (*N*-methyltetrahydropapaverine) yields veratraldehyde and a new base, 4 : 5-*dimethoxy*-2-*β*-*methylaminoethylbenzaldehyde*, $C_{12}H_{17}O_3N$. The chemical behaviour of this compound is very similar to that of cotarnine; it is colourless, but yields primrose-coloured salts, derived from 6 : 7-dimethoxy-2-methyl-3 : 4-dihydro*iso*quinolinium hydroxide by substitution. The addition of aqueous potassium cyanide to a solution of the chloride precipitates 1-*cyano*-6 : 7-*dimethoxy*-2-*methyltetrahydroiso*quinoline, $C_{13}H_{16}O_2N_2$, and boiling aqueous sodium hydroxide converts the aldehyde-base into the anhydrides of the corresponding acid and alcohol, 1-*keto*-6 : 7-*dimethoxy*-2-*methyltetrahydroiso*quinoline, $C_{12}H_{15}O_3N$, and 6 : 7-*dimethoxy*-2-*methyltetrahydroiso*quinoline, $C_{12}H_{17}O_2N$. The aldehyde-base yields an acetone condensation product, *bis*(4 : 5-*dimethoxy*-2-*β*-*methylaminoethylbenzylidene*)-*acetone*, $C_{27}H_{36}O_5N_2$.

***166. "The colour and constitution of azo-compounds." By John Theodore Hewitt and William Thomas.**

Further information regarding the colour exhibited by doubly substituted azo-compounds has been collected, and the following substances have been examined.

1. *p*-Acetylaminobenzeneazophenol.
2. *p*-Aminobenzeneazophenol and its dihydrochloride.
3. *p*-Dimethylaminobenzeneazophenol; its mono- and di-hydrochlorides and acetyl derivative.
4. *p*-Trimethylammonium iodide-benzeneazophenol.
5. *p*-Dimethylaminobenzeneazoanisole.
6. *p*-Trimethylammonium iodide-benzeneazoanisole.

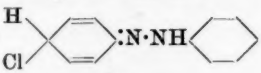
Substances 2, 3, 4, 5, and 6 give yellow solutions in neutral solvents; 2, 3, and 5 give red or magenta solutions in dilute hydrochloric acid (formation of monohydrochloride), whilst in concentrated hydrochloric acid the solutions become orange in colour (dihydrochloride—oxonium salt).

Solutions of 4 and 6 remain yellow in dilute acid, but give orange solutions like the other substances in concentrated acid.

Discussion.

Mr. Baly pointed out that there seemed to him to be certain objections to Dr. Hewitt's explanation of the origin of the increased

absorption of the hydrochlorides of the substituted azo-compounds. In the first place, it must be remembered that the addition of hydrochloric acid, if it be added to the molecule in the way suggested, must decrease the residual affinity of the molecule, and therefore it was difficult to understand how the absorption could thereby be increased, since the amount of absorption depended directly on the residual affinity of a compound. In the second place, the quinonoid structure advanced by Dr. Hewitt would not be expected to have so decidedly a deeper colour than the parent substance, since Mr. Tuck had shown that although there was a difference between the two isomeric compounds: $C_6H_5\cdot N{:}N\cdot C_6H_4\cdot OBz$ and $C_6H_5\cdot NBz\cdot N{:}C_6H_4{:}O$, yet this difference was in no way comparable with that between hydroxyazobenzene and its hydrochloride. In the third place, since azobenzene itself gave a hydrochloride far more deeply coloured than the parent substance, it would appear that any explanation of the colour of the hydrochlorides of the substituted azo-compounds must also be capable of explaining the similar phenomenon as observed with azobenzene itself. It was true that an analogous structure for azobenzene hydrochloride might be written:



but this appeared to be improbable.

About a year ago Miss Marsden and he showed that the aminoaldehydes and -ketones of the aromatic series displayed a great increase in absorption in the presence of a small quantity of hydrogen chloride in alcoholic solution, although the true hydrochlorides were colourless. Dr. Lapworth had suggested that this increase in colour might be due to the formation of an electro-positive ion, for example, $CHO\cdot C_6H_4\cdot\overset{+}{N}H_3$, where the nitrogen atom was quinquevalent, and so possessed an increased residual affinity. The hydrochloride (undissociated) would naturally be colourless, owing to the entire removal of the residual affinity of the amino-group. He (the speaker) suggested that possibly some analogous condition might obtain with the azo-grouping, and that a positive ion might be formed, thus: $C_6H_5\cdot\overset{+}{N}H{:}N\cdot C_6H_5$. The residual affinity of the azo-linking would then be increased, and the suggestion would have the merit of applying equally well to azobenzene and its substituted derivatives.

Dr. Hewitt, in reply, said that Dr. Lapworth's observation that the addition of alcoholic hydrochloric acid to alcoholic aminoazobenzene first produced an orange colour which afterwards turned purple, might be due to the transitory production of a salt of benzeneazophenylammonium, which was afterwards transformed into the quinonoid salt.

Mr. Baly's objection to the quinonoid formulæ for the salts was not supported by the chemical facts. Free benzeneazophenol behaved as a hydroxylic aromatic compound towards substituting agents, but in its salts with acids, the original phenolic nucleus resisted the action of nitric acid, but now was easily substituted in the other nucleus as if it were an anilide or hydrazone. Similar arguments could be brought forward with regard to the aminazo-compounds.

***167. "Studies of dynamic isomerism. Part IX. The relationship between absorption spectra and isomeric change. Absorption spectra of sulphonic derivatives of camphor." By Thomas Martin Lowry and Cecil Henry Desch.**

The band which is present in the absorption spectrum of α-bromocamphor appears also in the spectra of the ammonium π-sulphonate, the π-sulphonamide, and the acetyl derivative of this amide. It is also observed in the potassium β-sulphonate, the β-sulphonamide, the β-sulphonanhydramide, and the sulphopiperidide (m. p. 75°) derived from α-bromocamphor, but disappears when the two α-hydrogen atoms are displaced by halogens, as in dibromocamphor β-sulphonanhydramide. In the case of α-chlorocamphor, the band is also absent from the spectrum of the mono-substituted anhydramide, although it is developed by the β-sulphonamide and the potassium β-sulphonate. In the case of camphor and α-methylcamphor, the sulphonic acids and their salts give rise to a band, but the amide and anhydramide give continuous absorption curves. The absorption bands of the alkali-sulphonates are weakened by the addition of an excess of alkali, although this is an essential condition for bringing about isomeric change.

168. "*iso*Iminazolone."
By Henry John Horstman Fenton and W. A. R. Wilks.

When dry dihydroxymaleic acid is intimately mixed with excess of carbamide and the mixture is heated to 100°, three distinct products are obtained; one of these is a compound which is sparingly soluble in water, crystallises in the tetragonal system, and gives an intense red colour with ferric chloride. Analysis and molecular-weight determination show that this compound has the formula $C_3H_4ON_2$, and its mode of formation suggests the constitution: $\begin{matrix}CH\cdot NH\\ \|\\ CH\cdot NH\end{matrix}\!\!>\!CO$. It appears, however, to differ notably in many respects from the "μ-iminazolone" obtained by Marckwald and Ellinger (*Ber.*, 1892, **25**, 2357).

When evaporated with chlorine water, or with hydrochloric acid and a trace of potassium chlorate, *iso*iminazolone leaves a brilliant pink residue, which is changed to violet by ammonia. Its behaviour in this respect is indeed closely analogous to that of uric acid or xanthine, and it is considered probable that erroneous conclusions may have been arrived at by former investigators in placing too much reliance on this colour reaction as indicative of purine derivatives.

169. "Homologues of furfuraldehyde." By Henry John Horstman Fenton and F. Robinson.

The halogen derivatives of methylfurfuraldehyde are readily obtained by the action of dry halogen acids on ketohexoses, such as lævulose, or on various forms of cellulose (compare Fenton and Gostling, *Trans.*, 1899, **75**, 423; 1901, **79**, 807). The authors have studied the application of the Friedel and Crafts' reaction in effecting syntheses by these halogen derivatives, and further evidence is brought forward in support of the constitution previously assigned to these compounds.

Benzylfurfuraldehyde, $O<\begin{matrix}C(CH_2Ph):CH\\ C(CHO)=CH\end{matrix}$, obtained by the interaction of chloromethylfurfuraldehyde and benzene in presence of aluminium chloride, crystallises in large, colourless prisms, which melt at 31°. The *benzylphenylhydrazone* and the *oxime* are colourless and crystalline, and the latter has been obtained in two stereoisomeric forms.

Chloromethylfurfuraldehyde is easily oxidised by means of dilute nitric acid, yielding a dibasic acid, $C_4H_2O(CO_2H)_2$, which is identical with furan-2 : 5-dicarboxylic acid (dehydromucic acid).

170. "The relation between the strengths of acids and bases, and the quantitative distribution of affinity in the molecule. Part II." By Bernhard Flürscheim.

In Part I (*Trans.*, 1909, **95**, 718), it was mentioned that a few amines had affinity values which were not in agreement with the theory then published. In order to determine these anew, it was first necessary to improve Farmer and Warth's distribution method, since the results obtained by these authors sometimes differ considerably from those obtained by other methods, a fact which has been attributed by Lundén to possible association. Two new ways for determining volatile amines in the benzene layer have been worked out, one consisting in distilling off the benzene in a current of dry hydrogen chloride and heating the residue in a current

of the same gas; the other, in retaining the amine by a weighed amount of picric acid. The latter method was shown to reduce the experimental error to less than one milligram. Determinations in very dilute solution were thus rendered possible, giving, for *m*-toluidine, for instance, results in agreement with those obtained by Bredig by the conductivity method. In this way, the halogen-substituted anilines, previously disagreeing with the theory, were found to be in perfect harmony with the same, and thus to constitute another experimental proof in its favour.

171. "The oxidation of hydroxy-derivatives of benzaldehyde and acetophenone." By Henry Drysdale Dakin.

Ortho- and para-hydroxybenzaldehydes, when warmed with ammonia and hydrogen peroxide, readily give good yields of catechol and quinol respectively. Similarly, *o*- and *p*-hydroxyacetophenones yield the same products. The amount of hydroxybenzoic acid formed in both cases is quite insignificant. The corresponding *m*-hydroxy-derivatives, on similar treatment, undergo normal oxidation and yield *m*-hydroxybenzoic acid.

A number of other *o*- and *p*-hydroxy-derivatives were found to behave similarly on oxidation. 5-Nitro-2-hydroxybenzaldehyde gives nitrocatechol, and 4-hydroxy-3-methylbenzaldehyde and 2-hydroxy-4-methoxyacetophenone yield 2-methoxyquinol and 4-methoxyquinol respectively. Resacetophenone and 2 : 5-dihydroxyacetophenone probably react in the same manner, but the resulting trihydric phenols are too unstable in alkaline solution to be easily isolated.

If the hydroxyl group in the *o*- or *p*-hydroxybenzaldehyde and hydroxyacetophenone be replaced by a methoxy-, ethoxy-, nitro-, or amino-group, no formation of a phenol occurs, but usually a small yield of the corresponding benzoic acid is obtained.

A large number of methoxy-, ethoxy-, nitro-, and amino-derivatives of benzaldehyde and acetophenone, which did not contain a free hydroxy-group in the *o*- or *p*-position, were all found to yield the corresponding benzoic acids on oxidation. The yields were usually small, as these substances are much more resistant to the action of hydrogen peroxide than the *o*- and *p*-hydroxy-derivatives. The above results may be explained on the assumption that the salts of *o*- and *p*-hydroxybenzaldehydes and the *o*- and *p*-hydroxyacetophenones possess a quinonoid structure, as already suggested by Hantzsch in the case of some of the salts of *o*-hydroxybenzaldehyde (*Ber.*, 1906, **39**, 3081), and it also furnishes an explanation of the different behaviour on oxidation of the corresponding *m*-compounds, which presumably do not possess this structure.

The oxidation of *p*-hydroxybenzaldehyde may be represented in the following way :

$$O{:}C_6H_4{:}CH{\cdot}OH \longrightarrow O{:}C_6H_4{<}^{H}_{OH} + H_2CO_2 \longrightarrow HO{\cdot}C_6H_4{\cdot}OH.$$

172. "The intramolecular rearrangement of diphenylamine orthosulphoxides." By Edward de Barry Barnett and Samuel Smiles.

It was shown that the orthosulphoxides of diphenylamine are converted by the action of certain acid reagents into the orthoquinonoid derivatives of phenazothionium. The reaction has been studied with the tetranitro-, di-*p*-nitro-, *iso*dinitro-, and the unsubstituted sulphoxide, and it has been found that the change proceeds the more readily the stronger the basic properties of the quadrivalent sulphur. The last-named sulphoxide furnishes phenazothionium chloride.

173. "Double and triple ferrocyanides of magnesium, aluminium, and cerium with potassium and ammonium." By Frederic William Robinson.

The author has investigated the above salts in order to ascertain whether the triple salts are definite compounds or isomorphous mixtures of double salts.

Magnesium.—Salts of the composition $R_2MgFeC_6N_6$ (R being the alkali metal) have been obtained and their properties investigated. Salts of varying composition, $[RR_1]_2MgFeC_6N_6$, were produced under different conditions, the ratio R/R_1 varying according to the conditions of preparation.

Aluminium.—Salts of the composition $RAlFeC_6N_6,4H_2O$ were isolated, which, when dehydrated, are very similar to Prussian-blue. A series of triple salts, $[NH_4,K]AlFeC_6N_6$, was prepared, and when the alkali metal was in large excess, salts were obtained containing two equivalents of the alkali metal and two of aluminium per unit of acid radicle.

Cerium.—Crystalline double salts have been obtained possessing the composition $RCeFeC_6N_6$. They exhibit very similar phenomena both in their formation and properties to the analogous aluminium salts. The constitution of the triple cerium potassium ammonium salts has also been established.

174. "Action of Grignard's reagent on ethyl oxalate." By John Kenneth Harold Inglis and Alfred Sidell Mason.

In the hope of finding a convenient method of obtaining α-ketonic acids, the above action has been investigated. It was supposed that

by acting on the ester with magnesium ethyl halide the hydrolysis of the resulting additive product would yield propionylformic acid according to the following scheme:

$$(CO_2Et)_2 \longrightarrow CO_2Et\cdot CEt(OEt)\cdot OMgBr \longrightarrow CO_2Et\cdot CEt(OH)_2 \longrightarrow C_2H_5\cdot CO\cdot CO_2Et.$$

Magnesium ethyl bromide was therefore allowed to react with the dry ester in molecular proportions. After hydrolysis of the resulting mixture with dilute sulphuric acid and ice, the ethereal solution was dried and fractionally distilled under 25 mm. pressure. The acid boils at 74—78°/25 mm., and the ester at 74—77°/25 mm. Between 74° and 83° 12·5 grams of a pale yellow liquid were obtained, the theoretical yield for the ester being 65 grams. This liquid appeared to be a mixture of ester and acid. The oxime of the acid melted sharply at 154°, the melting point of α-oximinobutyric acid.

Similar experiments were carried out with magnesium phenyl bromide in the expectation of obtaining phenylglyoxylic ester. This ester boils at 151—154°/30—40 mm., and 18 grams of a yellow oil were obtained boiling between 140° and 160°, the theoretical amount being 89 grams. The phenylhydrazone of the acid was prepared and found to contain 11·86 per cent. of nitrogen (theoretical, 11·66); after recrystallisation from alcohol it melted at 147°. The attempt to isolate the acid was, however, unsuccessful.

The above results point to the possibility of preparing these two esters from oxalic ester. It is hoped to continue these experiments with a view to ascertain the conditions under which the yield may be increased.

175. "The partial racemism of menthyl *r*-mandelate."
By Alexander Findlay and Evelyn Marion Hickmans.

From a study of the solubility relations at 35°, 25°, 10°, and 0°, it has been found that *l*-menthyl *r*-mandelate is stable at these temperatures, and from a crystallisation experiment at −15°, it would appear that even at this temperature the transition point has not been reached, so that resolution of *r*-mandelic acid by crystallisation of its *l*-menthyl ester cannot be effected at temperatures above −15°. The transition point must lie below this, and has not been determined.

176. "The primary interaction of chlorine with acylanilides."
By Kennedy Joseph Previté Orton and William Jacob Jones.

It has been shown, by measuring the free chlorine in the solution, that chlorine and acylanilides (or chloroamines and hydrochloric acid)

in acetic acid solution enter into a reversible reaction, which is represented by the equation: $Ar{\cdot}NHAc + Cl_2 \rightleftharpoons Ar{\cdot}NClAc + HCl$. Equilibrium is attained extremely rapidly, but is gradually disturbed by the chlorination of the anilide (when that is possible) which follows slowly on the primary reaction.

The following table gives the extent of the reaction in various cases when the anilide and the chlorine are respectively in the first instance at a concentration of 0·025 gram-molecule per litre:

Anilide.	Percentage of chlorine combined in 75 per cent. acetic acid.	Percentage of chlorine combined in 90 per cent. acetic acid.	Percentage of chlorine combined in glacial acetic acid.
(*p*)$NO_2{\cdot}C_6H_4{\cdot}NHAc$.....	39·5	11	0
(2 : 4)$Cl_2{:}C_6H_3{\cdot}NHAc$	80	34	0
(2 : 4)$Cl_2{:}C_6H_3{\cdot}NH{\cdot}CHO$ ...	83·5	32	0
(2 : 4)$Cl_2{:}C_6H_3{\cdot}NHBz$	62	14	0
(*s*)$Br_3{:}C_6H_2{\cdot}NHAc$	86	43	0

The measurements in 90 per cent. acetic acid lead to an equilibrium constant, but in 75 per cent. no constant can be calculated. In 65 per cent. acetic acid, a constant is obtained if the reaction is represented as: $Ar{\cdot}NHAc + Cl_2 \rightleftharpoons Ar{\cdot}NClAc + H^{\cdot} + Cl'$, that is, the equilibrium constant is proportional to the square of the concentration of the hydrochloric acid.

It will be seen that the primary reaction between the anilide and the chlorine does not occur to a measurable extent in glacial acetic acid; nevertheless, in the presence of a molecular proportion of sodium acetate, more than 90 per cent. of the chlorine reacts. In 50 per cent. acetic acid, on the other hand, there was only a trace of free chlorine.

The method of estimating the free chlorine, which requires only two to three minutes, consists in the aspiration of a small volume of air through the solution, such that about 5 per cent. of the free chlorine is extracted. Comparison with experiments made with standard solutions of chlorine gives the measure of free chlorine. With the apparatus which the authors have elaborated, the measurements can be made with a high degree of accuracy, the differences in the value of the free chlorine in two similar experiments never exceeding 0·05 c.c. of *N*/10 thiosulphate.

177. "The quantitative decomposition of the anilides: a study in steric influence." By Oliver Charles Minty Davis.

A series of experiments have been carried out on the quantitative hydrolysis of the anilides by means of sodium hydroxide.

The object of the research was to investigate the effect of orientation in the selected compounds on their chemical reactivity.

A considerable number of anilides were experimented on, and the main result of the work is to show that under the conditions chosen by the author the chief effect of substituent elements and groups (and their position in the molecule) is to influence the rate of decomposition.

178. "Note on the anomalous viscosity of nitrobenzene." By Ferdinand Bernard Thole.

In support of his theory of "motcisomerism" (*Ber.*, 1907, **40**, 508), Knoevenagel quoted the results obtained by Mühlenbein with regard to the viscosity of nitrobenzene.

Mühlenbein (*Diss.*, Cöthen, 1901) stated that the viscosity of freshly distilled nitrobenzene decreased by 0·7 per cent. on standing for some hours. This he attributed to a change in the configuration of the nitro-group. He also drew attention to the fact that specimens of quinoline derived from various sources possess widely different densities and viscosities. The boiling points of the specimens used, however, seemed to show that these were by no means sufficiently pure to give trustworthy physical constants.

Repetition of Mühlenbein's work on nitrobenzene does not confirm his results.

The mean results of four series of observations using nitrobenzene from various sources are as follows:

	Immediately after distillation.	After 22 hours.
Mean density (25°/4°)	1·19870	1·19869
Mean viscosity (25° C.).....	0·018226	0·018224

The mean difference in viscosity, namely, 0·012 per cent., is well within the limits of experimental error.

The carefully purified quinoline used (b. p. 235°) had a density of 1·08994 and a viscosity of 0·033724. Mühlenbein obtained densities varying between 1·08228 and 1·09351, and viscosities between 0·033911 and 0·045405.

The Viscosity of Ethyl Acetoacetate.—Schaum (*Ber.*, 1898, **31**, 1964) and Dunstan and Stubbs (Trans., 1908, **92**, 1919) have pointed out that the physical constants of freshly distilled ethyl acetoacetate change on keeping the ester for some time. A closer study of this change has been carried out, and curves have been plotted showing the change of viscosity and density with time.

The viscosity and density are found to increase rapidly at first, and then more slowly, until equilibrium is attained. Extrapolation gives a density of, approximately, 1·02045 and a viscosity of 0·015210 for the ester immediately after distillation.

The low initial viscosity shows that the freshly distilled liquid exists almost entirely in the ketonic form.

179. "**Studies of the carbonates. Part I. The equilibrium between calcium carbonate and carbonic acid.**" By **Clarence Arthur Seyler and Percy Vivian Lloyd.**

Schlössing's law has been verified by means of double titration with methyl-orange and phenolphthalein as indicators.

The following general law has been established in the case of waters containing calcium chloride and sulphate, sodium bicarbonate, chloride, and sulphate, and magnesium sulphate in quantities such as occur in fresh natural waters. "When a water is in equilibrium with the limestone which it percolates, the square of the alkalinity is directly proportional to the free carbonic acid and inversely to the total hardness." The alkalinity and hardness being expressed in gram-equivalents per litre and corrected for degree of ionisation, the constant has the value $F + 10^{-6}$, where F is on the average 113.

The constant F is called the "saturation factor" of the water, and is a criterion as to whether the water is saturated or not with the limestone.

For mineral water or sea-water the factor would be higher.

For different forms of calcium carbonate (calcite and arragonite) the factor F is proportional to the "solubility product" and to the square of the solubility in pure water.

180. "**Some esters of arsenious acid. Part II. Resorcinyl arsenite.**" By **William Robert Lang and John Obins Woodhouse.**

Continuing the experiments described in a previous communication (Lang, MacKey, and Gortner, *Trans.*, 1908, **93**, 1364), but using one of the dihydric phenols, quantities by weight of resorcinol and of arsenious oxide corresponding with the equation below were heated to the melting point of the former in a distilling flask, connected through a weighed flask with an exhaust pump. The temperature was kept constant, and the arsenic slowly dissolved in the melted resorcinol, yielding an amber-coloured fluid becoming darker as the heating progressed, the pressure being 60 mm. The water evolved in the reaction, $3C_6H_4(OH)_2 + As_2O_3 = (C_6H_4O_2)_3As_2 + 3H_2O$, collected in the trap and was weighed as a check, due precautions being taken to prevent loss. After heating for fifty-five minutes the mixture was allowed to cool, broken up, and extracted

with hot toluene, which removed from it some resorcinol. The residue was dissolved in dry ethyl alcohol, in which these esters are soluble, when an immediate precipitate of arsenious oxide was produced. Analysis of the substance obtained on evaporation in a vacuum of the alcoholic extract proved it to contain from 5 to 6 per cent. of arsenious oxide in excess of that required by the formula $(C_6H_4O_2)_3As_2$, showing that arsenious oxide dissolved in the ester formed. To prevent this, an excess of resorcinol was employed, namely, 100 grams, and 50 grams of arsenious oxide heated with it as before, the proportions of the former to the latter being, according to the equation supposed to represent the reaction, 100 to 60; in this way an amount of resorcinol corresponding with 10 grams of arsenious oxide would, of necessity, remain unacted on and be readily extracted from the ester by a specific solvent. After an hour's heating, the solidified mass was broken up and digested in a reflux condenser with dry toluene, which extracted a considerable proportion of resorcinol. This treatment was repeated until no more resorcinol could be obtained on evaporation of the solvent. The resorcinol-free mass was analysed as follows. About 1 gram was treated with water, which caused its immediate decomposition, the solution acidified with hydrochloric acid, and the arsenic precipitated as sulphide, dried on a tared filter, and weighed. The results of numerous analyses, which closely corresponded, gave:

Found, As = 31·9. $C_{18}H_{12}O_6As_2$ requires As = 31·65 per cent.

Resorcinyl arsenite closely resembles hardened gelatin in appearance, melts at 24°, and has a specific gravity of 1·9. It is soluble in methyl, ethyl, propyl, and butyl alcohols, but insoluble in ether, chloroform, benzene, or toluene. Water, however, immediately decomposes it.

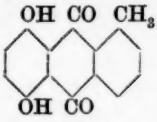
The same experiments were tried with quinol, but, so far, without success.

181. "The constitution of chrysophanic acid and of emodin." (Preliminary note.) By Frank Tutin and Hubert William Bentley Clewer.

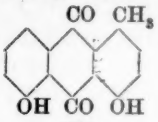
It was considered highly probable by Jowett and Potter (*Trans.*, 1903, **83**, 1327) that chrysophanic acid is represented by formula (I), and that emodin differed from this compound by the presence of one additional hydroxyl group.

By a comparison of the properties of quinizarin and 2-methylquinizarin respectively with those of chrysophanic acid, the present authors have obtained conclusive proof that the last-mentioned com-

pound does not contain the quinol grouping. There is reason to believe, furthermore, that chrysophanic acid is represented by formula (II), that is to say, that it is 1-*methylchrysazin*. Emodin



(I.)



(II.)

will then be, in all probability, a *hydroxy*-1-*methylchrysazin*, but the position of the additional hydroxyl group is at present uncertain.

The work is being continued, and it is hoped to obtain further evidence in support of the above conclusions, which, if they are correct, indicate that chrysophanic acid is very closely related to both aloe-emodin and rhein (compare Robinson and Simonsen, *Proc.*, 1909, 26, 76).

182. "**The morphotropic relationships between the derivatives of picric acid.**" **By George Jerusalem.**

The author has prepared a number of salts of picric and styphnic acids with primary, secondary, and tertiary amines and quaternary ammonium bases, and has determined their crystallographic constants. The discussion of the data thus obtained shows that the crystalline forms of these substances all fall into the scheme devised by Barlow and Pope; a considerable amount of quantitative confirmation of the correctness of the structure assigned to benzene by these authors has thus been collected.

The author further shows that the molecular volumes of the salts in question are directly proportional, within limits of + or − 4 per cent., to the sums of the valencies composing the molecular complexes. Further confirmation is thus provided of the conclusion that each atom in a compound substance appropriates a portion of the total volume directly proportional to its fundamental valency.

183. "**A possible intramolecular change in the inactive phenylalkyloxyacetic acids.**" **(Preliminary note.) By William Ernest Stephen Turner.**

Attention has already been drawn to the steady decrease occurring, as dilution proceeds, in the values of the dissociation constants of phenyl-methoxy-, -ethoxy-, and -propoxy-acetic acids (Findlay, Turner, and Owen, *Trans.*, 1909, **95**, 939).

The author has found that aqueous solutions of phenylpropoxyacetic

acid become yellow on keeping for a long period, and deposit a yellow solid from which, by means of ether, pale yellow, needle-shaped crystals, m. p. 144°, have been obtained. Moreover, in the liquid state, carefully purified samples of the ethoxy- and propoxy-acids deposit yellow needles at a very slow rate.

The crystals isolated from the liquid propoxy-acid consist of two substances, the main constituent melting at 152°. Physico-chemical experiments show that whereas these crystals have the same molecular weight as phenylpropoxyacetic acid, they differ from it in constitution.

Owing to the slow rate at which it proceeds, and the consequent difficulty of accumulating materials, the exact nature of the change occurring cannot yet be determined.

184. "The colour and constitution of diazonium salts. Part I." By Gilbert T. Morgan and Mary Alcock.

The diazonium salts of benzoyl-1 : 4-naphthylenediamine, which are stable coloured substances, have now been compared with the corresponding derivatives of benzoyl-*p*-phenylenediamine and its alkylated homologues.

Benzoyl-p-*aminobenzenediazonium chloride* and the corresponding *nitrate*, *sulphate*, *perchlorate*, and *acetate* are also remarkably stable, but colourless when freshly prepared. as-*Benzoylmethyl*-p-*phenylenediamine* and as-*benzoylethyl*-p-*phenylenediamine*, colourless needles, m. p. 153—154° and 117° respectively, give rise to colourless, oily diazonium salts with the commoner mineral acids; their *diazonium molybdates* and *tungstates* are, however, solid and colourless.

The conclusion is drawn that the absence of colour in the diazonium salts of benzoyl-*p*-phenylenediamine and its homologues, and the presence of colour in the corresponding series of diazo-derivatives from benzoyl-1 : 4-naphthylenediamine, is dependent on the differences between the chromogenic properties of the benzene and naphthalene nuclei respectively, rather than to any variation in the structure of the diazonium complex contained in the coloured salts derived from the naphthalene base.

The foregoing diazonium salts couple with the undiazotised base in the usual way to form diazoamines, such as the compound

$$C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_5,$$

but when treated with aqueous sodium hydroxide or ammonia they lose a portion of the diazo-nitrogen and yield diazo-oxides, as, for example, $C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot O\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_5$.

185. "The hydrolysis of amygdalin by acids. Part I." By James Wallace Walker and Vernon K. Krieble.

A comparative examination has been made of the action of dilute and concentrated hydrochloric and sulphuric acids as well as of concentrated aqueous oxalic and trichloroacetic acids on amygdalin. It is found that, whilst concentrated hydrochloric acid first attacks the nitrile radicle, producing *l*-amygdalinic acid, a solution of sulphuric acid of corresponding strength liberates *l*-mandelonitrile. Oxalic acid behaves in a manner similar to dilute hydrochloric, but trichloroacetic acid does not hydrolyse amygdalin at all under the same conditions of temperature and concentration at which hydrochloric acid readily effects the hydrolysis.

186. "Some derivatives of anthraquinone." By Dorothy Harrop, Roland Victor Norris, and Charles Weizmann.

The authors have prepared a number of derivatives of 1 : 2-, 1 : 3-, and 1 : 4-dimethylanthraquinone. By the action of sulphuric and boric acids on the dichlorodimethylbenzoylbenzoic acids produced by condensing 1 : 4 dichlorophthalic anhydride with the three xylenes in presence of aluminium chloride, the corresponding dichlorodimethylanthraquinones are obtained. The chlorine atoms in the latter compounds are easily displaced, and the corresponding dianilino-, diphenoxy-, and dithiophenoxy-derivatives have been isolated.

The following note has been received since the meeting :—

187. "Isomeric derivatives of phosphoric acid." By Frederic Stanley Kipping and Bernard Dunstan Wilkinson Luff.

Many salts prepared by combining phenyl-*p*-tolylphosphoric acid, $PO(OPh)(O{\cdot}C_6H_4Me){\cdot}OH$, with an optically active base have been examined, but so far all attempts to resolve the acid have been unsuccessful. Nevertheless, evidence that the acid is a mixture of isomerides has been obtained by treating phenyl-*p*-tolylphosphoric chloride with asymmetric bases (compare Kipping and Hall, *Trans.*, 1901, **79**, 442). With *dl*-hydrindamine, for example, the chloride yields a mixture of two isomeric hydrindamides, $PO(OPh)(O{\cdot}C_6H_4Me){\cdot}NH{\cdot}C_9H_9$, one of which melts at 97—99°, the other at about 81—83°; similarly with *d*-hydrindamine, or with *l*-menthylamine, the chloride gives two isomeric amides. The more sparingly soluble compound is readily

isolated in all three cases, but the more readily soluble one, which seems to form half of the original product, is not easily obtained free from its isomeride.

These results seem to prove that phenyl-*p*-tolylphosphoric acid is an externally compensated compound, and further experiments on the resolution of this and of similar derivatives of phosphoric acid are in progress.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Blair, *David.* A grammar of the principles and practice of chemistry. pp. vi + 255. ill. London 1815. (*Recd.* 3/6/09.)
From Mr. A. H. Coote.

Lister Institute of Preventive Medicine. Collected papers, No. 5. London 1908. (*Reference.*) From the Director.

II. *By Purchase.*

Delbrück, *Max.* [*Editor.*] Brauerei-Lexikon. Lief 1. pp. 80. ill. Berlin 1909. (*Reference.*)

Diergart, *Paul.* [*Editor.*] Beiträge aus der Geschichte der Chemie dem Gedächtnis von Georg W. A. Kahlbaum. pp. xv + 652. ill. Leipzig 1909. (*Recd.* 17/6/09.)

Hinrichsen, *F. W.* Die Untersuchung von Eisengallustinten. (Die chemische Analyse, Vol. VI.) pp. 140. Stuttgart 1909. (*Recd.* 9/6/09.)

Kahlbaum, *Georg W. A.* See **Diergart**, *Paul.*

Kremann, *R.* Ueber die Anwendung der thermischen Analyse zum Nachweis chemischer Verbindungen. (Sammlung, Vol. XIV.) Stuttgart 1909. (*Recd.* 10/6/09.)

Law, *Edward F.* Alloys and their industrial applications. pp. xvi + 269. ill. London 1909. (*Recd.* 22/6/09.)

Marchlewski, *L.* Die Chemie der Chlorophylle und ihre Beziehung zur Chemie des Blutfarbstoffs. pp. x + 187. ill. Braunschweig 1909. (*Recd.* 17/6/09.)

Naske, *Carl.* Die Portland-Zement-Fabrikation. 2nd edition. pp. vii + 410. ill. Leipzig 1909. (*Recd.* 17/6/09.)

Richter, *Victor von.* Chemie der Kohlenstoffverbindungen oder organische Chemie. Edited by *R.* **Anschütz** and *G.* **Schroeter**. Vol. I. Die Chemie der Fettkörper. 11th edition. pp. xx + 793. Bonn 1909. (*Reference.*)

Schucht, *Ludwig.* **Die Fabrikation des Superphosphats, mit Berücksichtigung der anderen gebräuchlichen Düngemittel.** 3rd edition. pp. viii + 460. ill. **Braunschweig 1909.** (*Recd.* 17/6/09.)

THE LIBRARY.

The Library will be closed for Stocktaking from **Monday, August 9th,** until **Saturday, August 21st,** 1909, inclusive.

Fellows are particularly requested to return all Library Books in their possession **not later than Wednesday, August 4th.**

LIST OF FELLOWS, 1909.

The List of Fellows for 1909 is now in active preparation, and changes of address received after 31st July cannot be included in it.

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

The next Ordinary Meeting will be held on **Thursday,** October 21st, 1909, at **8.30** p.m., when the **Mendeléeff Memorial Lecture** will be delivered by **Professor W. A. Tilden, F.R.S., Past President.**

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 30/10/09.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 360.

The following are abstracts of papers received during the vacation and published or passed for publication in the *Transactions*:

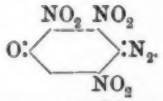
188. "The action of bromo*cyclo*hexane and of 4-bromo-1-methyl*cyclo*-hexane on the sodium derivative of ethyl malonate." By Edward Hope and W. H. Perkin, jun. (Trans., 1909, 1360.)

The authors have prepared *ethyl* cyclo*hexylmalonate* and *ethyl* 1-*methyl*cyclo*hexyl*-4-*malonate* by the above reactions; the properties of these substances and their derivatives are described.

189. "2 : 3 : 5-Trinitro 4-aminophenol and derivatives." By Raphael Meldola and James Gordon Hay. (Trans., 1909, 1378.)

This compound has been isolated by the careful hydrolysis of the acetyl derivative by means of sulphuric acid. It crystallises from acetic acid in deep red needles decomposing at about 145°. The most important conclusion deduced from the study of the substance is that the loss of a nitro-group on diazotisation is primarily due to the mobility conferred by the presence of a methoxy-group, since the present compound, although highly nitrated and possessing a nitro-group in a most favourable position for elimination, can be diazotised with the retention of all its nitro-groups, the diazonium sulphate

passing at once on dilution with water into 2 : 3 : 5-trinitroquinonediazide :



The 3-nitro-group of this compound is capable of being replaced by hydroxy- and alkyloxy-groups without the removal of the diazo-group.

190. "Colour and constitution of azo-compounds. Part IV." By John Theodore Hewitt and Ferdinand Bernard Thole. (Trans., 1909, 1393.)

In order to obtain more insight into the relationship between constitution and selective absorption, the following bisazo-compounds of relatively simple type have been prepared and examined.

Benzeneazobenzeneazodimethylaniline, m. p. 190° (uncorr.), and its hydrochloride, $C_{20}H_{19}N_5$,HCl; *o*-tolueneazo-*o*-tolueneazodimethylaniline, m. p. 138° (uncorr.), and its hydrochloride, $C_{22}H_{23}N_5$,HCl; benzeneazobenzeneazophenol, m. p. 180° (uncorr.); benzeneazobenzeneazophenyl acetate, m. p. 178° (uncorr.).

The absorption of these substances in acid solutions has been examined for the visible part of the spectrum. The dimethylamino-compounds dissolve in concentrated sulphuric acid with a red colour, passing to blue on dilution; the blue solutions correspond with the salts of a mono-acid base. The phenolic compound dissolves in concentrated sulphuric acid with a fine purple colour, dilution producing complete hydrolysis.

191. "The amygdalins. Part I."
By J. Wallace Walker and Vernon K. Krieble. (Trans., 1909, 1437.)

The study of the action of traces of alkali on *l*-amygdalin, first observed by one of the authors (Walker, *Trans.*, 1903, **83**, 472), has been continued, and a partial resolution of the racemised solution has been effected. The equilibrium between the different varieties has been found to be unaffected by changes in the concentration and nature of the alkali, or in the concentration of the amygdalin, or by temperature. The great difference in the action of emulsin on the several modifications shows, however, that a further change takes place in the racemised solution on heating, and renders it doubtful whether the crystalline material separated from the racemised solution contains *d*-amygdalin or an isomeric substance.

192. "The action of the Grignard reagent on phthalic esters." By Yūji Shibata. (Trans., 1909, 1449.)

The author has studied the action of the Grignard reagent on phthalic esters, and finds that, in spite of the close analogy of phthalic acid to succinic acid, the action of the Grignard reagent on phthalic esters differs from that on succinic esters in producing derivatives of phthalide, instead of glycols. More frequently, the reaction proceeds one step further, with the production of derivatives of phthalane. 1 : 1-*Dimethyl-3-methylenephthalane*, 1 : 1-*diphenyl-3-phenylenephthalane*, and 1 : 1-*dibenzyl-3-benzylidenephthalane* have thus been obtained. Of the various space formulæ proposed for benzene from time to time, that of Graebe, which represents Kekulé's well known formula in space, accounts most satisfactorily for the results obtained in this investigation.

193. "Constitution of hydroxyazo-compounds. Part II. Action of mercuric acetate on benzeneazonaphthols." By Alec Duncan Mitchell and Clarence Smith. (Trans., 1909, 1430.)

In continuation of former work (*Trans.*, 1908, **93**, 842), the action of mercuric acetate on hydroxyazo-compounds of the naphthalene series in alcohol has been examined. Benzeneazo-β-naphthol does not react with the salt, whilst benzeneazo-α-naphthol undergoes oxidation to Witt and Dedichen's $\beta\beta$-dinaphthyl derivative (*Ber.*, 1897, **30**, 2660). When the β-position contains a substituent, the oxidation is prevented and monomercuriacetates are formed.

β-Benzeneazo-α-naphthol mercuriacetate, $C_6H_5\cdot N_2\cdot C_{10}H_5(OH)\cdot Hg\cdot CO_2\cdot CH_3$, m. p. 208° (decomp.), is a red powder sparingly soluble in the usual solvents, except glacial acetic acid; by prolonged boiling with the latter, the mercuriacetate group is replaced by hydrogen. *4-Nitro-2-benzeneazo-α-naphthol mercuriacetate*, $C_6H_5\cdot N_2\cdot C_{10}H_4(OH)(NO_2)\cdot Hg\cdot CO_2\cdot CH_3$, m. p. 221—222°, is a dull red powder obtained from *4-nitro-2-benzeneazo-α-naphthol*, m. p. 178—179°, which crystallises in dark red needles and forms an *acetate*, m. p. 208°, crystallising in orange-yellow needles. *2-Nitro-4-benzeneazo-α-naphthol mercuriacetate* is a lustrous, reddish-brown substance, which blackens on heating, but does not melt below 290°; it is obtained from *2-nitro-4-benzeneazo-α-naphthol*, m. p. 164°, which crystallises in orange-red needles, and forms an *acetate*, m. p. 173°, crystallising in red prisms. *Bisbenzeneazo-α-naphthol mercuriacetate*, $(C_6H_5\cdot N_2)_2C_{10}H_4(OH)\cdot Hg\cdot CO_2\cdot CH_3$, m. p. 235—239° (decomp.), separates from phenol generally as a dark purplish-brown mass, but on

one occasion was obtained in black bronzy needles. 2′ : 4′ : 6′-*Tribromo*-2-*nitro*-4-*benzeneazo*-α-*naphthol*, m. p. 216°, orange-yellow plates, 2′ : 4′ : 6′-*tribromo*-4-*nitro*-2-*benzeneazo*-α-*naphthol*, m. p. 215—216°, orange-red needles, and *bis*-2′ : 4′ : 6′-*tribromobenzeneazo*-α-*naphthol*, m. p. 249—253°, a maroon powder, have also been prepared.

194. "Preparation of the acyl derivatives of the aldehydecyanohydrins. Part I." By Francis Francis and Oliver Charles Minty Davis. (Trans., 1909, 1403.)

It has been found that aromatic aldehydes readily react with acid chlorides in the presence of aqueous potassium cyanide to form the acyl derivatives of the corresponding cyanohydrins. The reaction may be generalised and expressed as follows :

$$R{\cdot}CHO + R'{\cdot}COCl + KCN \longrightarrow R{\cdot}CH(O{\cdot}COR'){\cdot}CN + KCl.$$

195. "The action of phosphorus pentachloride on the methylene ethers of catechol derivatives. Part V. Derivatives of protocatechuyl alcohol and protocatechuonitrile." By Arthur James Ewins. (Trans., 1909, 1482.)

No dichloromethylene derivative can be isolated by the direct action of phosphorus pentachloride on piperonyl alcohol (Barger, *Trans.*, 1908, **93**, 567); the corresponding chloride, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2Cl$ (Decker and Koch, *Ber.*, 1905, **38**, 1739), however, readily yields 3 : 4-dichloromethylenedioxybenzyl chloride, $CCl_2{:}O_2{:}C_6H_3{\cdot}CH_2Cl$, b. p. 154—156°/16 mm., which is transformed by formic acid into 3 : 4-carbonyldioxybenzyl chloride, $CO{:}O_2{:}C_6H_3{\cdot}CH_2Cl$, m. p. 57° (compare Pauly and Alexander, *Ber.*, 1909, **42**, 2350). By boiling 3 : 4-carbonyldioxybenzyl chloride with water, an impure crystalline catechol derivative free from chlorine was obtained (protocatechuyl alcohol ?).

By a similar series of reactions, piperonylonitrile yields successively 3 : 4-dichloromethylenedioxybenzonitrile, $CCl_2{:}O_2{:}C_6H_3{\cdot}CN$, b. p. 155—156°/15 mm., m. p. 76—77°, 3 : 4-carbonyldioxybenzonitrile, $CO{:}O_2{:}C_6H_3{\cdot}CN$, prisms from benzene, m. p. 112°, and 3 : 4-dihydroxybenzonitrile (protocatechuonitrile), $C_6H_3(OH)_2{\cdot}CN$, needles from water, m. p. 152°.

By the action of phosphorus pentachloride on 3 : 4-methylenedioxymandelamide, $CH_2{:}O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$ (Barger and Ewins, *Trans.*, 1909, **95**, 555), and boiling the product with formic acid, 3 : 4-methylenedioxyphenylglyoxylonitrile, $CH_2{:}O_2{:}C_6H_3{\cdot}CO{\cdot}CN$, was obtained.

The abnormal reaction between piperonyl alcohol and phosphorus pentachloride is due to the condensation, under the influence of phosphorus halides, of the piperonyl chloride first produced to a substance, $C_{16}H_{12}O_4$, m. p. above 360°, which sublimes under diminished pressure, and is probably related to anthracene. Its formation may be expressed by the equation :

$$2CH_2{:}O_2{:}C_6H_3{\cdot}CH_2Cl = CH_2{:}O_2{:}C_6H_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C_6H_2{:}O_2{:}CH_2 + 2HCl.$$

A crystalline *nitro*-derivative of the probable composition

$$C_{16}H_{10}O_4(NO_2)_2$$

was obtained.

196. "The preparation of disulphides. Part VI. Note on a new method of preparing disulphides." By Thomas Slater Price and Douglas Frank Twiss. (Trans., 1909, 1489.)

Although alkyl thiosulphates do not react with iodine at the ordinary temperature, reaction readily takes place at higher temperatures, the corresponding disulphides being formed according to the equation : $2KO{\cdot}SO_2{\cdot}SR + 2H_2O + I_2 = R_2S_2 + 2KHSO_4 + 2HI$. The yield of disulphide is practically quantitative. The preparation of benzyl disulphide, *o*-nitrobenzyl disulphide, and dimethyl dithiodiglycollate is described.

197. "Halogen derivatives of cinnamic acid." By Thomas Campbell James and John Joseph Sudborough. (Trans., 1909, 1538.)

Further experiments have been made on the addition of bromine to methyl and ethyl cinnamate.

The action of alkalis on *d*- and *l*-cinnamic acid dibromides and on methyl and ethyl *allo*cinnamate dibromides has been studied, and also the action of various organic bases on cinnamic acid dibromide.

Attempts have been made to resolve α-bromo- and α-bromo-*allo*-cinnamic acids into optically active components, but without success.

198. "The conversion of pinene into sobrerol." By George Gerald Henderson and Wilfred James Stevenson Eastburn. (Trans., 1909, 1465.)

Not only the mixture of *d*- and *l*-pinene obtained from American oil of turpentine, but also *d*-pinene and *l*-pinene themselves yield the inactive modification of sobrerol when oxidised with aqueous mercuric

acetate by the method formerly described, and therefore optical inversion occurs in the process.

Using the formation of sobrerol as a test, the presence of *d*-pinene in a specimen of Russian oil of turpentine has been proved, whilst a sample of Swedish oil of turpentine gave a negative result.

199. "Influence of various sodium salts on the solubility of sparingly soluble acids. Part II." By James Charles Philip and Frederick Basil Garner. (Trans., 1909, 1466.)

The work described in an earlier paper (*Trans.*, 1905, **87**, 987) has been extended. In harmony with what was then found, the authors find that the weaker the acid from which the sodium salt is derived, the greater is the influence of the salt on the solubility of benzoic, salicylic, *o*-chlorobenzoic, and *m*-nitrobenzoic acids. It is further found that if of two sparingly soluble acids the weaker is also the more soluble, then under the influence of any sodium salt the solubility of the stronger acid is increased to a greater extent than that of the other. The experimental figures for the solubility are compared with those calculated by Noyes' formula, and the agreement between the two sets of values is generally good.

200. "Organic derivatives of arsenic. Part II. Triaminotriphenylarsine oxide and tricamphorylarsinic acid." By Gilbert T. Morgan and Frances M. G. Micklethwait. (Trans., 1909, 1473.)

Triaminotriphenylarsine oxide, $O{:}As(C_6H_4{\cdot}NH_2)_3$, was produced by condensing aniline and arsenious chloride in boiling benzene or toluene, and treating the mixture with aqueous alkali.

Tricamphorylarsinic acid, $(C_{10}H_{15}O)_3As(OH)_2$, was isolated from the products of the interaction of sodium camphor and arsenious chloride.

201. "The estimation of arsenic in organic compounds." By Harry F. V. Little, Edward Cahen, and Gilbert T. Morgan (Trans., 1909, 1477.)

The compounds were heated with sodium peroxide and sodium carbonate, the acidified aqueous extract of the fusion boiled with potassium iodide, and the arsenic precipitated as sulphide. The precipitate was re-dissolved in aqueous sodium hydroxide, and the solution treated with hydrogen peroxide. After acidifying and

boiling to decompose the excess of peroxide, the reduction with potassium iodide was repeated, the liberated iodine boiled off, and the resulting arsenious solution neutralised and titrated with standard iodine solution.

202. "A method of harmonising the atomic weights." By James Moir.

The author assumes the cause of valency to be the presence, in varying numbers, of a sub-element of atomic weight 1/112, and regards the main bulk of the mass of the elements as due to polymerisation of an entity consisting of the hydrogen atom, less the above aggregation; thus if the fraction 1/112 be represented by μ, a bivalent element contains 2μ, and denoting the entity referred to by $\overline{H}$, the atomic weight of oxygen, for example, $=16\overline{H}+2$. By the application of this idea, close agreement is found between the calculated and observed values for the atomic weights of the elements.

203. "The spontaneous crystallisation of solutions of sodium carbonate and sodium thiosulphate." By Bernard Mouat Jones. (Trans., 1909, 1672.)

The author has determined the conditions under which spontaneous crystallisation takes place in the systems sodium carbonate-water and sodium thiosulphate-water when solutions of these salts, freed from crystal nuclei, are slowly cooled (or warmed) with constant shaking in the presence of glass fragments. In the first system, solutions of concentration of from 0 to 48 parts of anhydrous salt to 100 parts of water, on cooling and shaking, give crystals of ice or decahydrate at definite temperatures. These give rise to well-defined supersolubility curves intersecting in a "hypertectic" point at $-7{\cdot}6°$, and running roughly parallel to the corresponding solubility curves.

The solubility of the monohydrate has a negative temperature-coefficient, and saturated solutions therefore have to be warmed in order to bring about crystallisation of this salt. A supersolubility curve for this phase has been traced. At higher temperatures it becomes practically coincident with the solubility curve, since the latter is almost parallel to the temperature axis.

Of the fourteen possible solid phases which may separate out from solutions of sodium thiosulphate, only two, ice and the secondary monohydrate, give rise to definite supersolubility curves. When

dilute solutions of concentrations between 0 and 40 parts anhydrous salt to 100 parts of water are slowly cooled and shaken, ice separates out at definite temperatures. With concentrated solutions between concentrations of 179 and 255, under the same conditions, the secondary monohydrate always appears at definite temperatures.

The spontaneous crystallisation of anhydrous salt, primary dihydrate, and primary and secondary pentahydrates has been observed in solutions kept at rest for long periods.

204. "The effect of contiguous unsaturated groups on optical activity. Part II. Acids containing two adjacent ethenoid groups." By Thomas Percy Hilditch. (Trans., 1909, 1570.)

An effort has been made to determine the effect of two conjugated ethylenic bands on the optical activity of an organic compound by means of the study of active esters and salts of acids containing this system, together with their reduction products. Derivatives of muconic, sorbic, piperic, cinnamylidenemalonic, and the corresponding $\alpha\beta$- and $\beta\gamma$-dihydro- and tetrahydro-acids have been examined in this way, with the following results:

(1) In all cases the compound possessing two contiguous ethenoid linkings shows a very marked optical exaltation with respect to either the monoethylenic or the fully saturated acids.

(2) As previously observed in other instances, the monoethylenic derivatives possess greater rotatory power than the saturated compounds, but the anomaly is of a much smaller order than that due to the conjugated system.

(3) The phenyl group in the δ-position with respect to carboxyl appears to exert a depressing influence on optical rotatory power.

(4) Adipic acid, although fully saturated, shows distinct exaltation of rotatory power in its optically active esters and salts.

(5) Muconic acid derivatives, possessing a structure symmetrical with respect to the centre of the conjugated system, show the most enhanced anomaly of all.

205. "The effect of contiguous unsaturated groups on optical activity. Part III. The normal series of fatty dibasic acids." By Thomas Percy Hilditch. (Trans., 1909, 1578.)

The dimenthyl esters and dibrucine salts of the acids from oxalic to sebacic inclusive have been prepared and examined polarimetrically in chloroform solution.

The oxalic derivatives show a very pronounced exaltation of optical

activity; the malonic and succinic compounds show a depression below the normal value, similar to that previously noted in the case of formic and acetic acid compounds; and, finally, adipic acid shows a distinct exaltation, although not so great as in oxalic acid. The glutaric compounds and derivatives of the higher acids are all approximately normal.

It is suggested that, whilst the anomaly in the case of oxalic acid is obviously due to the contiguity of two carboxyl groups, the cause of the enhanced values of dimenthyl and dibrucine adipates may be the contiguity of the carboxyl groups in space, which, according to the usually accepted stereochemical views, would occur in adipic acid and its derivatives.

206. **"The formation at high temperatures of some refractory metals from their chlorides."** **By John Norman Pring and William Fielding.** (Trans., 1909, 1497.)

The authors have investigated the reactions whereby some refractory metals can be prepared by exposing the vapour of their volatile chlorides to electrically heated carbon rods or filaments.

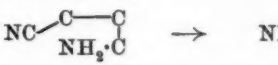
With tungsten chloride, used alone, under diminished pressure, decomposition took place in contact with the carbon rod at temperatures between 1200° and 1500°, and with molybdenum, below 1300°, forming adherent deposits on the rods of the pure metals. Above these temperatures the carbides resulted. In presence of small quantities of water vapour, the metals were always obtained free from the carbides.

Boron and silicon were obtained from their chlorides by exposing these together with hydrogen to the heated carbon rods. Pure crystalline silicon was obtained at temperatures between 1700° and 1850°. A thin protective layer of the carbide which first formed on the rod prevented carbonisation of the subsequent deposit, until, at a temperature of about 1900°, the carbide alone resulted.

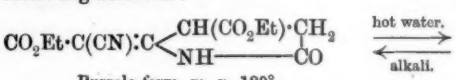
With boron, the deposit always consisted of the carbide (B_6C), which was formed at temperatures between 1800° and 2000°. Some approximate photometric measurements were made on the radiating properties of the metal-coated rods. A very large increase in the luminosity for a given power-expenditure was observed with tungsten and molybdenum, amounting to about three times that of the carbon, whilst very little difference was produced by the deposits of silicon and boron carbide.

207. "The formation and reactions of imino-compounds. Part X. The formation of imino-derivatives of pyrrole and of *iso*pyrrole from amino-nitriles." By Stanley Robert Best and Jocelyn Field Thorpe. (Trans., 1909, 1506.)

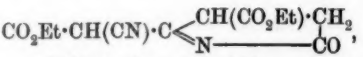
The authors have discovered that open-chain compounds having an amino-group in the γ-position with respect to a nitrile group, pass on treatment with sodium ethoxide into derivatives of pyrrole in accordance with the scheme:



It is also found that those ketones, derived from these imino-compounds, which have a carbon atom adjacent to the nitrogen, doubly linked outside the ring, tend readily to pass into the isomeric compound having the bond in the ring, the two compounds being mutually convertible the one into the other. This is shown by the following formulæ:

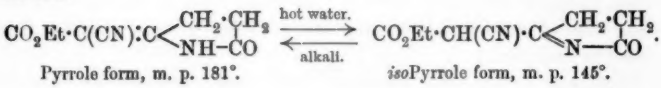


Pyrrole form, m. p. 129°.



*iso*Pyrrole form, m. p. 109°.

and also



Pyrrole form, m. p. 181°. *iso*Pyrrole form, m. p. 145°.

208. "The atomic weight of chlorine." By Robert Whytlaw Gray and Frank Playfair Burt. (Trans., 1909, 1633.)

The value for the weight of a normal litre of hydrogen chloride resulting from twenty-one experiments is 1·63915 grams, Lat. 45°. The value previously published (*Proc.*, 1908, **24**, 215) was slightly too low.

Two volumes of hydrogen chloride, when decomposed by red-hot aluminium in a specially constructed apparatus, were found to yield 1·0079 volumes of hydrogen, the gases being measured at 0° and 760 mm. Eight experiments were made, and the maximum deviation was 1 part in 5000.

The atomic weight of chlorine calculated from these numbers,

assuming that the atomic weight of hydrogen is 1·00762 (Morley) and that the density of hydrogen is 0·089873 gram per litre at 0° and 760 mm., Lat. 45°, is 35·459 ; O = 16.

The authors have also measured the form of the *pv* isothermal of hydrogen chloride at 0° between the pressure limits of 800 and 160 mm. The amounts of gas absorbed by the glass surfaces of the apparatus at different pressures were experimentally determined, and the observed *pv* values were corrected. Similar measurements with oxygen were also made in the same apparatus. Graphic extrapolation gave for the mean coefficient of compressibility between 1 and 0 atmosphere pressure at 0° :

for oxygen..... $A'_0 = 0{\cdot}000964$,
,, hydrogen chloride ... $A'_0 = 0{\cdot}00748$,

for the molecular weight of hydrogen chloride on the oxygen standard, 36·469, and for the atomic weight of chlorine, 35·461. The value of the atomic weight resulting from the volumetric analysis, namely, 35·459, is thus confirmed.

It is hence concluded that 35·460 is a close approximation to the true atomic weight of chlorine.

209. "*iso*Quinoline derivatives. Part II. The constitution of the reduction products of papaverine." By Frank Lee Pyman. (Trans., 1909, 1610.)

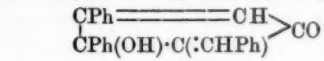
Goldschmiedt (*Monatsh.*, 1886, **7**, 485; 1898, **19**, 324) obtained by the reduction of papaverine a crystalline base melting at 200—201° which he termed "tetrahydropapaverine," together with an amorphous base from which no crystalline derivative was obtained.

The author has shown that this amorphous base is identical with the "*iso*tetrahydropapaverine" obtained by Freund and Beck (*Ber.*, 1904, **37**, 3321) by the reduction of papaveraldine, and is in reality *tetrahydropapaverine*. It forms crystalline salts of the formula $C_{20}H_{25}O_4N,HX$, and yields an *N-benzoyl* derivative, which gives on oxidation a new base, 6 : 7-*dimethoxy*-3 : 4-*dihydroisoquinoline*. The methochloride of this is identical with 6 : 7-dimethoxy-2-methyl-3 : 4-dihydro*iso*quinolinium chloride, a salt obtained by the action of hydrochloric acid on 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde (prepared by the oxidation of laudanosine : compare Pyman, *Trans.*, 1909, **95**, 1266). Further proof that the amorphous base is tetrahydropapaverine is afforded by the fact that it yields laudanosine on methylation.

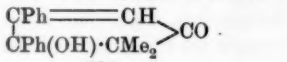
Analyses of Goldschmiedt's so-called "tetrahydropapaverine" and its derivatives show that this base has the formula $C_{20}H_{23}O_4N$, and is in reality 1 : 2-*dihydropapaverine*.

210. "Direct proofs of the presence of the hydroxyl group in derivatives of anhydroacetonebenzil." By Francis William Gray.

The author has succeeded in acetylating benzylideneanhydroacetonebenzil (I) and $\beta\beta$-dimethylanhydroacetonebenzil (II) with acetic

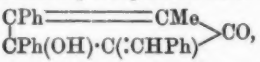


(I.)



(II.)

anhydride containing sulphuric acid. For the formation of an acetyl derivative of the anhydroacetonebenzil series, it is essential that both hydrogen atoms of the methylene group should be displaced, but in the case of benzylidene-α-methylanhydroacetonebenzil,

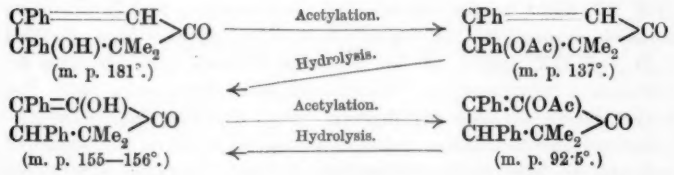


no acetyl compound but a dehydration derivative is obtained.

Direct proof of the presence of the hydroxyl group in α-methylanhydroacetonebenzil and in benzylidene-α-methylanhydroacetonebenzil was afforded by the preparation of their ethyl ethers. The conclusion is drawn, that ethyl ethers can be obtained by the method used (boiling with ethyl alcohol and sulphuric acid) only with compounds in which the hydrogen atom of the CH group of anhydroacetonebenzil is displaced by a methyl group.

211. "Isomerides of anhydroacetonebenzil and its derivatives." By Francis William Gray.

The acetyl derivatives of $\beta\beta$-dimethylanhydroacetonebenzil and benzylideneanhydroacetonebenzil (see preceding paper) on hydrolysis give isomerides of these compounds. The reactions may be represented as follows:



212. "The constitution of glucose derivatives. Part II. Condensation derivatives of glucose with aromatic amino-compounds." By James Colquhoun Irvine and Robert Gilmour. (Trans., 1909, 1545.)

In continuing their previous work (*Trans.*, 1908, **93**, 1429) on the constitution of sugar derivatives, the authors have condensed glucose

with a number of aromatic amino-compounds, obtaining mutarotatory stereoisomeric forms of glucose-*p*-toluidide, glucose-β-naphthylamide, glucose-*p*-phenetidide, and glucose-*o*-carboxyanilide.

The compounds mentioned undergo mutarotation comparable in every way with that shown by glucoseanilide, for which the γ-oxidic structure has been established by a synthetical method. The results indicate that all the compounds must be similarly constituted, and that, so far as the cases examined are concerned, the normal condensation of glucose with amino-acids or bases consists in the elimination of water from the amino-group and the hydroxyl group attached to the terminal carbon atom of the sugar molecule.

The following compounds were isolated in pure stereochemical forms:

*α-Glucose-*p*-toluidide*: anhydrous prisms, $[\alpha]_D^{20}$ +181·9° ⟶ −45·0.

*β-Glucose-*p*-toluidide*: needles containing $1H_2O$, $[\alpha]_D^{20}$ −97·6° ⟶ −45·2; plates containing $\frac{1}{2}H_2O$, $[\alpha]_D^{20}$ −94·6° ⟶ −47·3.

*β-Glucose-*p*-phenetidide*: needles containing $1H_2O$, $[\alpha]_D^{20}$ −96·1° ⟶ −38·3.

β-Glucose-β-naphthylamide: needles containing $1H_2O$, $[\alpha]_D^{20}$ −118·7° ⟶ −48·1.

α-Glucose-o-carboxyanilide: needles containing $1H_2O$, $[\alpha]_D^{20}$ +87·4° ⟶ +14·5.

213. "The relation between viscosity and chemical constitution. Part IV. Viscosity and hydration in solution." By Albert Ernest Dunstan and Ferdinand Bernard Thole. (Trans., 1909, 1556.)

The authors have determined the viscosity-concentration curves for the binary systems composed of water and methyl, ethyl, and propyl alcohols, and acetic acid respectively at different temperatures. They confirm the results of previous investigators, and discuss the nature of the mixtures of maximum viscosity, particularly with respect to the temperature-coefficient of viscosity.

214. "Some derivatives of *l*-benzoin." By Henry Wren. (Trans., 1909, 1583.)

d-Mandelamide and *d*-benzoin have been isolated and found to agree in their properties with *l*-mandelamide and *l*-benzoin. A number of optically active derivatives of *l*-benzoin have also been prepared.

215. "Racemisation phenomena observed in the study of *l*-benzoin and its derivatives." By Henry Wren. (Trans., 1909, 1593.)

It has been shown that *l*-benzoin and its methyl ether readily racemise under the action of potassium hydroxide or sodium ethoxide,

this being probably due to a desmotropic change within the molecule. *l*-Benzoin ethyl ether was found to be partly, and carbanilido-*l*-benzoin completely, racemised by heat, whilst under the action of benzoyl chloride at a rather high temperature, of aniline at 100°, and of a saturated solution of hydrogen chloride in alcohol at a temperature not exceeding 40°, *l*-benzoin has been converted into derivatives of *r*-benzoin.

Finally, methyl *l*-mandelate has been found to undergo partial racemisation during its conversion into *l*-mandelamide by the action of alcoholic ammonia. The acetylation of *l*-benzoin-α-oxime has also been effected.

216. "Diketodiphenylpyrroline and its analogues." By Siegfried Ruhemann. (Trans., 1909, 1603.)

The author has continued his work on the interaction of the sodium derivatives of aromatic amides with ethyl phenylpropiolate (*Trans.*, 1909, **95**, 984), and has prepared a number of analogues of diketodiphenylpyrroline, $\begin{matrix}CO—CO\\ |\quad\quad |\\ CPh{:}CPh\end{matrix}>NH$. These substances have a deep colour, which varies from dark red to brown and black, and have the property in common that they dissolve in dilute alkalis to yield blue solutions, which, however, rapidly turn yellow. They resemble, therefore, isatin, and, like this form, phenylhydrazones and oximes.

In this connexion the author has examined the behaviour of phenylcarbamide and *p*-tolylcarbamide towards ethyl phenylpropiolate, and has found that this reaction, unlike that in which carbamide is used, does not give rise to cyclic compounds, but colourless acyl derivatives of carbamide, for example, phenylpropiolylphenylcarbamide, $C_6H_5{\cdot}C{:}C{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.

217. "The synthesis of acridines: tetramethylacridines, dimethylnaphthacridines, naphthaquinacridines, diquinacridines." By Alfred Senier and Arthur Compton. (Trans., 1909, 1623.)

By further employment of the methods described in a previous paper (*Trans.*, 1907, **91**, 1927), the authors have obtained 2 : 3 : 7 : 8-*tetramethylacridine*, and also the corresponding 9 : 10-*dimethylpheno*-$\begin{matrix}N\text{-}\beta\\ |\\ CH\text{-}\alpha\end{matrix}$-*naphthacridine* and 9 : 10-*dimethylpheno*-$\begin{matrix}N\text{-}\alpha\\ |\\ CH\text{-}\beta\end{matrix}$-*naphthacridine*. The chief object of this inquiry, however, was to prepare acridines with heterocyclic wings, and three heterocyclic acridines, namely, $\begin{matrix}6\text{-}N\text{-}6\\ |\\ 5\text{-}CH\text{-}5\end{matrix}$-*diquinacridine*, $\begin{matrix}\alpha\text{-}N\text{-}6\\ |\\ \beta\text{-}C\text{-}5\end{matrix}$-*naphthaquinacridine*, and $\begin{matrix}\beta\text{-}N\text{-}6\\ |\\ \alpha\text{-}CH\text{-}5\end{matrix}$-*naphthaquinacridine*, have been isolated by the use of aminoquinolines.

The diquinacridine described is the first known member of a group of twenty-one possible isomeric diquinacridines derived from ordinary quinoline, and, similarly, the two naphthaquinacridines belong to a group of heterocyclic acridines of which eighteen members are theoretically possible.

All these compounds, containing as they do the acridine fluorphoric group, exhibit marked fluorescence. When dissolved in the usual organic solvents, the ultraviolet waves are so reduced in refrangibility that they appear in the blue, whereas in solution in glacial acetic or concentrated sulphuric acids they are reduced as far as the green, or even yellowish-green, portion of the spectrum.

Thursday, October 21st, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

Messrs. D. F. Blyther and G. J. Woods were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Jehangir Dhanjishaw Anklesaria, Ahmedabad, India.
James Alexander Hadden Armstrong, Dumisa, Natal.
Donald William Elsom Barker, 2, Hope Street, Wrexham.
Harold Baron, B.Sc., 21, Underhill Road, East Dulwich, S.E.
Stanley Robert Best, M.Sc., Hope Villa, Wellington Road, Whalley Range, Manchester.
Hubert Frederick Bottomley, The Cedars, Wavertree Road, South Woodford.
Henry Shaw Breakspear, B.A., 20, Walton Well Road, Oxford.
Oskar K. H. Burger, Ph.D., 4, Mission Row, Calcutta.
Frank Ward Bury, B.Sc., Lyndale Cottage, Darwen.
William Edward Callister, B.Sc., The Rowans, Onchan, I.O.M.
William Gordon Carey, Wyngarth, Harpenden.
Lakshami Chand, B.A., B.Sc., c/o Messrs. Ramchand and Bulaki Nandan Sahni Street, Benares, U.P., India.
James Ferguson Dawson, B.Sc., Glencoe House, Tarbert, Loch Fyne, N.B.
Alfred Charles Dunningham, B.Sc., 28, Victoria Road, Northwich.
Edward Charles Edgar, D.Sc., Dalegarth, Romiley, Cheshire.
Alfred Edge, Ravenhurst, Clayton Bridge, Manchester.

Frederick Watson Edwards, 64, Coppice Side, Swadlincote.
Arthur James Ewins, B.Sc., 7, Towton Road, West Norwood, S.E.
George Peters Forrester, 69, Beck Strasse, Darmstadt.
William Adolf Freymuth, Rangoon, Burma.
Otto Fürstenhagen, 28, Schlesische Strasse, Berlin.
George Pomeroy Furneaux, B.A., Harbour View, Brixham, S. Devon.
Henry Dent Gardner, jun., M.Sc., Fairmead, The Goffs, Eastbourne.
Victor John Harding, M.Sc., Lonsdale Terrace, Whitefield, Manchester.
Arthur John Harvey, 88a, East India Dock Road, Poplar, E.
Robert Douglas Hendry, 3, Glebe Terrace, Alloa.
William Cudmore McCullagh Lewis, M.A., Garmoyle, Bangor, Ireland.
Carl Olof Lundholm, 2, Eton Avenue, Hampstead, N.W.
Roland Victor Norris, M.Sc., 1, Howe Street, Higher Broughton, Manchester.
Charles Proud, 12, Chancellor Road, Southend-on-Sea.
Walter Ritchings, M.Sc., 89, Rosehill Road, Burnley.
Pindi Das Sabherwal, Bhera, Punjab.
Manindra Sinha, B.A., St. Xavier's College, Calcutta.
Spencer Boyd Cortis Stanford, Glenwood, Dalmuir, Dumbartonshire.
Guy Stephenson, Alexandra Terrace, Crook, Co. Durham.
George Bertram Stones, M.Sc., Bank Villas, Tyldesley, nr. Manchester.
James Thallon Strachan, 10, Nelson Street, Sunderland.
Hubert Sanderson Tasker, B.A., Emmanuel College, Cambridge.
Joseph Grantley Tingle, Nauru, Marshall Islands, Central Pacific.
Henry Thomas Tizard, B.A., 23, Geneva Road, Kingston-on-Thames.
Herbert Turner, B.Sc., 217, Middleton Street, Moss Side, Manchester.
Nikolai Waliaschko, Hohenzollernstr, 12, II, 1, Leipzig.
Charles Weizmann, Ph.D., D.Sc., 57, Birchfields Road, Rusholme, Manchester.
Herbert Ernest Williams, 70, Wellington Road, Charlton, Kent.
Roland Francis Young, c/o Taquah Mining and Exploration Co., Tarkwa, Gold Coast.

Professor WILLIAM A. TILDEN, D.Sc., F.R.S., then delivered the Mendeléeff Memorial Lecture, at the conclusion of which a vote of thanks was proposed by Sir EDWARD THORPE, C.B., F.R.S., seconded by Sir WILLIAM RAMSAY, K.C.B., F.R.S., and carried by acclamation.

218. "Carthamine." (Preliminary note.) By T. Kametaka and Arthur George Perkin.

Carthamine, the red colouring matter of safflower (*Carthamus tinctoria*), was first isolated by Schlieper (*Annalen*, 1846, **58**, 362) as a red, amorphous powder possessing a cantharides iridescence, and to this he assigned the formula $C_{14}H_{16}O_7$. Radcliffe (*J. Soc. Dyers*, 1897, **13**, 158) obtained carthamine from safflower extract as red, iridescent needles melting at 168—169° (provisional), but did not analyse this product. The authors corroborate the work of Radcliffe, but regard the compound he prepared as a salt of carthamine, rather than the free colouring matter itself. They find that the crystalline substance is most readily obtained from the extract by means of pyridine and water, but that an elaborate purification is necessary to obtain a pure compound free from calcium, magnesium, and potassium salts. It forms red, iridescent needles, which, when dried at 110°, are exceedingly hygroscopic and are decomposed at about 228—230°. Analyses indicate that the formula of carthamine is probably $C_{15}H_{14}O_7$ (Found: C = 58·16; H = 4·87). On fusion with potassium hydroxide, carthamine gives *p*-hydroxybenzoic acid, as stated by Malin (*Annalen*, 1865, **136**, 117), but in the pure condition the dyestuff appears to be much more stable than has been previously suggested.

219. "A theory regarding the configuration of certain unsaturated compounds; and its application to the metallic ammines and the cinnamic acids." By Sarah Martha Baker.

According to the author's theory, if there is sufficient attraction between the other atoms joined to a nitrogen atom and that to which it is doubly bound, there are two possible isomerides, namely, the "*en*" isomeride, in which the other atoms are grouped round the double bond, and the "*ex*" or symmetrical isomeride. This theory has been extended to phosphorus, sulphur, and finally, in rare cases, to carbon compounds.

To represent the metallic ammines, it is assumed that the ionisable acid groups are connected to the metal through a chain of one or more $\cdot NH_3\cdot$ groups; but that the non-ionisable acid groups are directly joined to the metal, and, in most cases, prevented from undergoing ionisation by having an NH_3 group also attached, thus: $\cdot M\cdot X{:}NH_3$. Wherever the grouping $\cdot X{:}NH_3$ occurs there is a possibility of isomerism. An attempt was made to deduce the configuration of the *flavo*- and *croceo*-cobalt salts in terms of this theory.

Applying the same principles to the three cinnamic acids, it was shown that, if ordinary cinnamic acid is represented as "*ex*" fumaroid, *iso*cinnamic acid as "*ex*" maleoid, and *allo*cinnamic acid as "*en*" maleoid cinnamic acid, many of the anomalies in their behaviour are explicable.

220. "The relation between the chemical constitution of monoazo-dyes and their fastness to light." By Edwin Roy Watson.

The author puts forward the theory that the fading in light of an azo-dye is due to the oxidation of that part of the molecule which contains hydroxy- or amino-groups, and that the fastness of such a dye is increased by introducing into the phenolic or arylamino-part such other groups as will reduce the tendency to become oxidised.

221. "The influence of gaseous oxides of nitrogen on the rate of interaction of chlorine and hydrogen." By David Leonard Chapman and Patrick Sarsfield MacMahon.

It was shown that the brown gas resulting from the interaction of nitric oxide and chlorine—presumably nitrogen peroxide—inhibits the union of hydrogen and chlorine in the light. The inhibitor is slowly absorbed by the chlorine water in the actinometer, and as it is removed the electrolytic gas gradually recovers its original sensitiveness; the removal of the last trace of inhibitor appears to be facilitated by the action of light.

The retardation observed with nitrous oxide was so small that the authors conclude that this gas behaves as a diluent only. In this respect it resembles nitrogen and carbon dioxide.

222. "Estimation of small quantities of ferrous iron by potassium permanganate in the presence of hydrogen chloride." By John Albert Newton Friend.

The author has recently shown (*Trans.*, 1909, **95**, 1228) that, if certain precautions are rigidly observed, ferrous iron may be accurately estimated by titration with $N/10$-permanganate in the presence of any concentration of hydrogen chloride not exceeding $m/4$. Experiments have now been performed in a similar manner with $N/25$-permanganate and correspondingly smaller quantities of iron. The results are given in the table, the volume titrated being in each case 200 c.c.:

Concentration of hydrogen chloride.	Titre in c.c. $KMnO_4$.	Error, c.c.	0·5 gram $MnSO_4,5H_2O$. Titre in c.c. $KMnO_4$.	Error, c.c.	1·0 gram $MnSO_4,5H_2O$. Titre in c.c. $KMnO_4$.	Error, c.c.	2·0 grams $MnSO_4,5H_2O$. Titre in c.c. $KMnO_4$.	Error, c.c.
m/∞ ..	23·58	—	23·48	—	23·78	—	23·78	—
$m/8$ ..	23·86	0·28	23·52	0·04	23·79	0·01	23·78	0·00
$m/4$ ..	23·90	0·32	23·57	0·09	23·83	0·05	23·80	0·02
$3m/8$..	23·96	0·38	23·60	0·12	23·87	0·09	23·85	0·07
$m/2$ ..	24·12	0·54	23·80	0·32	23·93	0·15	23·88	0·10

The most satisfactory titrations were those obtained in the presence of from 1 to 2 grams of manganous sulphate, when the concentration of the hydrogen chloride did not exceed $m/4$. In general it was found that 1 gram of manganous sulphate was preferable to 2 grams, as, in the latter case, the end-point is less permanent, and with larger quantities is fugitive and therefore uncertain. As the presence of manganous sulphate slightly affects the value of the titration of ferrous sulphate in the absence of hydrogen chloride, it is important to standardise the permanganate with ferrous sulphate in the presence of the same amount of manganous sulphate as will be used in the hydrogen chloride solution.

The chief difficulty is to recognise the end-point, but with a little practice results sufficiently accurate for most purposes can be obtained in daylight, as is evident from a consideration of the above table. Commercial permanganate gave equally good results as the specially pure salt.

223. "The mutarotation of glucose and its nitrogen derivatives." By Robert Gilmour.

The author showed that the optical behaviour of the glucosephenylhydrazones (Behrend and Lohr, *Annalen*, 1908, **362**, 78) brings them into line with glucose-anilide, *p*-toluidide, and other similar compounds which possess the γ-oxidic structure.

On the analogy of the relationship between the specific rotations of the glucoses and the methylglucosides, the value for α-glucose-*p*-toluidide can be calculated (a_D +226°), and the calculated value is not widely different from the value found experimentally (a_D +181°). The values for α-glucose-*p*-phenetidide and -β-naphthylamide have been similarly calculated. The fact that tetramethyl glucoseanilide has the rotation a_D +224° lends support to the idea that α-glucoseanilide has also a high dextrorotation, since it is known that the introduction of four methoxyl groups into the glucose residue has little effect on the optical rotatory power.

It is suggested that the glucosephenylhydrazones possess the γ-oxidic

structure, and should thus exist in not more than two stereoisomeric interconvertible forms, having rotations of $\alpha_D + 224°$ and $-87°$ respectively.

The author considers that the mutarotation of glucose and its nitrogen derivatives is due to the presence of a labile hydrogen atom (shown in heavy type) which is not directly united to carbon,

$$\mathbf{H}\cdot C\cdot O\cdot \mathbf{H} \qquad\qquad H\cdot C\cdot \overset{\mathbf{H}}{\underset{\downarrow}{N}}\cdot C_6H_5,$$

and that the change occurs through the intermediate formation of an unstable aldehydic form. It seems probable that, under ordinary conditions, the γ-oxidic form of glucoseoxime is the more stable; but that under a particular set of conditions, the aldehydic form may be the more stable.

224. "The solubility of bismuth trisulphide in alkali sulphides and of bismuth trioxide in alkali hydroxides." By Joseph Knox.

The author finds that dried precipitated bismuth sulphide dissolves in solutions of both sodium and potassium sulphides, and that the solubility increases rapidly with the concentration of the alkali sulphide. The solubility in potassium sulphide is rather greater than in sodium sulphide of the same concentration. The addition of alkali hydroxides to the alkali sulphide solutions greatly increases the solubility of bismuth sulphide. In a solution of sodium disulphide the solubility of bismuth sulphide is about one-third of that in the corresponding strength of the monosulphide, whilst in solutions of ammonium sulphide and of alkali hydrosulphides and hydroxides, bismuth sulphide is insoluble.

From these facts it is shown that the solubility of bismuth sulphide in alkali sulphide solutions must depend on the formation of a complex anion with the sulphur ion of these solutions.

Bismuth trioxide dissolves to a slight extent in alkali hydroxides, the solubility being approximately proportional to the concentration of the alkali hydroxide. Towards strong bases it therefore behaves as the anhydride of a weak acid, but to a much less extent than the corresponding oxides of arsenic and antimony.

225. "Substituted amides of tartaric acid." By Kate Maud Jackson and Allen Neville.

The following new substituted amides of tartaric acid have been obtained, and as some of them illustrate the influence of constitution on the rotatory power of substances, their specific rotations are recorded.

Two determinations of the rotatory power of each substance were made, 1 per cent. solutions in pyridine being used:

	Melting point.	$[\alpha]_D^{15°}$.	$[M]_D^{15°}$.
Tartarodi-o-*anisidide*	180°	155·71	558·25
		155·83	560·78
Tartarodi-p-*anisidide*	about 250 (with decomposition)	205·80	740·88
		203·60	732·96
Tartarodi-p-*xylidide*	209°	148·87	529·97
		149·61	532·61
Tartarodi-m-4-*xylidide*	179	201·16	716·12
		199·98	711·93
Tartarodi-ψ-*cumidide*	240 (with decomposition)	168·42	646·73
		168·66	647·65

The substances were in all cases prepared from ethyl tartrate and the amine by heating to about 150° on an oil-bath for several hours. It will be seen that, in the case of the anisidides and xylidides, as in the case of similar isomeric compounds described by Frankland and Slator (*Trans.*, 1903, **83**, 1349), the effect of constitution is very marked. In the case of para- and ortho-compounds, the para has here, as in previously-described compounds, the higher rotatory power, whilst in the xylidides the *m*-4-compound has a considerably greater rotatory power than the *p*-compound.

Attempts have been made to prepare similar compounds from the different nitroanilines, but so far without success.

226. "A volumetric process for the estimation of tungsten." By Edmund Knecht and Eva Hibbert.

The process is based in the first instance on the well-known fact that tungstic acid is reduced by zinc and hydrochloric acid to tungsten dioxide, which, in presence of excess of acid, yields a clear light brown solution. If now a solution of a ferric salt be added, the dioxide is oxidised to the trioxide. The end-point is perceived by the disappearance of the intense blue colour of the intermediate compound corresponding with tungsten pentachloride, the reaction

$$Fe_2O_3 + WO_2 = 2FeO + WO_3$$

being quantitative. It is thus possible to estimate tungsten volumetrically in presence of iron. Potassium thiocyanate may also serve as indicator, but does not offer any particular advantage.

227. "The volumetric estimation of mercury, and the estimation of silver in presence of mercury." By Joseph Knox.

The thiocyanate method of Rupp and Kraus (*Ber.*, 1902, **35**, 2015) for the estimation of mercury in a solution of mercuric nitrate has been tested, and found to be both rapid and accurate.

The author showed that the estimation of silver by Gay-Lussac's method in presence of mercuric nitrate (by Rupp and Kraus' method) is impracticable, and described a volumetric method which depends on the solubility of silver chloride in potassium cyanide, but the gravimetric estimation of the silver is recommended as being more accurate and convenient. The accuracy of the latter method has been proved in a considerable number of determinations, in which the quantity of mercuric nitrate present was varied greatly.

228. "The rapid electro-analytical deposition and separation of metals. Part III." (Preliminary note.) By Henry Julius Salomon Sand.

A method for the analysis of alloys of copper and tin by electrolysis has been described by A. Fischer (*Zeitsch. Elektrochem.*, 1909, **15**, 591), in which an acid tartrate solution is employed in a similar manner as in the copper–bismuth separation given by the author (Trans., 1907, **91**, 395). It is stated by Fischer that the tin exerts a retarding influence on the copper, necessitating a higher potential for the complete deposition of the latter than in solutions from which tin is absent. In the experiments now described, however, no retarding action due to the tin has been observed. The copper may be precipitated completely from boiling solutions at an auxiliary potential of 0·60 volt, just as in the absence of tin. On the other hand, when chlorides are present, these exert a retarding influence varying with the amount of the chloride. This is due to the intermediate production by the current of more or less complex, very slightly dissociated cuprous compounds, which require a high potential for their reduction. The explanation of Fischer's result is to be sought, not in the presence of the tin, but in the fact that it was added by him as stannic ammonium chloride.

The author has separated copper from antimony under similar conditions to those employed for bismuth. The antimony should be present for the greater part in the antimonic state. In the analysis of an alloy, a suitable solution is obtained by employing a hot mixture of dilute nitric and tartaric acids as a solvent, and afterwards neutralising the free mineral acid.

229. "Some mercury derivatives of camphor." By James Ernest Marsh and Robert de Jersey Fleming Struthers.

A detailed description was given of work of which a preliminary account has already appeared (*Proc.*, 1907, **23**, 246; 1908, **24**, 267).

230. "The reduction of perchlorates by titanous salts." By Edmund Knecht.

In a recent paper by Rothmund, the reduction of perchlorates by titanous sulphate is discussed, and a method is described for the quantitative estimation of perchlorates, which is based on the complete reduction of the perchlorate by titanous sulphate, followed by the estimation of the resulting chloride by Volhard's process. Rothmund states that it should be possible to effect the estimation of perchlorates by ascertaining, by titration with iron alum, the amount of titanous sulphate that has been oxidised, but no experimental data are given.

Criticising Rothmund's results, Stähler maintains that the latter procedure is liable to give rise to serious errors, since, according to his finding, boiling alone is sufficient to convert some of the titanous into titanic salt.

It is now shown that, under suitable conditions, accurate results can be obtained by first reducing the perchlorate with titanous chloride, and then titrating back with standard iron alum, using potassium thiocyanate as indicator. For the successful carrying out of the titration, it is necessary to use the titanous chloride in a concentrated form and to acidify strongly with a mixture of sulphuric and oxalic acids.

231. "Further syntheses of *p*-hydroxyphenylethylamine." By George Barger and George Stanley Walpole.

The isolation of *p*-hydroxyphenylethylamine,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2,$$

an active principle of ergot, was recently described (Barger, *Trans.*, 1909, **95**, 1123), together with its preparation by the reduction of *p*-hydroxyphenylacetonitrile; two other syntheses have now been carried out.

First, benzoylphenylethylamine, $C_6H_5\cdot CH_2\cdot CH_2\cdot NHBz$, is nitrated, the *p*-nitro-compound is reduced, the amino-compound converted into the hydroxy-compound by the diazo-reaction, and the benzoyl group is finally removed by heating with acids; instead of the benzoyl, the corresponding acetyl and benzylidene derivatives may be employed.

Secondly, *p*-methoxyphenylpropionamide,

$$MeO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2,$$

is prepared from anicaldehyde; Hofmann's reaction then furnishes

p-methoxyphenylethylamine, from which the methyl group is eliminated by heating with acids.

A number of intermediate compounds were also described.

232. "The constitution of hydroxyazo-compounds. Part II." By William Bradshaw Tuck.

The absorption spectra of the *o*-hydroxyazo-compounds and their ethers have been compared with ortho-substituted phenols in which the substituting group contains a double bond in a position analogous to the double bond in the hydroxyazo-compounds. The effect of progressively increasing the degree of unsaturation attached to the azo-benzene nucleus has been investigated. The results obtained confirm the conclusions previously arrived at, and also indicate the reason for the apparently large difference between the absorption spectra of hydroxyazo-compounds and those of their sodium salts.

233. "Optically active substances containing no asymmetric atom. 1-Methyl*cyclo*hexylidene-4-acetic acid." By William Henry Perkin, William Jackson Pope, and Otto Wallach.

A detailed description was given of work of which a preliminary account has already appeared (this vol., 83).

234. "*iso*Quinoline derivatives. Part III. The oxidation of substituted 1-benzyltetrahydro*iso*quinolines." By Frank Lee Pyman.

The results obtained by the oxidation of narcotine, hydrastine, laudanosine, *N*-benzoyltetrahydropapaverine, tetrahydropapaverine, *N-ethyltetrahydropapaverine*, *N-propyltetrahydropapaverine*, 1-benzylhydrocotarnine, 1-ethylhydrocotarnine, 1-propylhydrocotarnine, and 1-benzyl-2-methyltetrahydro*iso*quinoline appear to justify the following general conclusions:

(1) That substituted 1-benzyltetrahydro*iso*quinolines suffer oxidation and fission simultaneously under the influence of hot dilute sulphuric acid and manganese dioxide, yielding the aldehyde corresponding with the substituted benzyl group, and a basic degradation product.

(2) That in the case of substituted 1-benzyl-2-alkyltetrahydro*iso*quinolines, the basic product is a substituted 2-β-alkylaminoethylbenzaldehyde, which yields salts of the corresponding 2-alkyl-3:4-dihydro*iso*quinolinium hydroxide.

(3) That in the case of substituted 1-benzyl-2-acyltetrahydro*iso*quinolines, and 1-benzyltetrahydro*iso*quinolines containing a free imino-group, the basic product is a substituted 3 : 4-dihydro*iso*quinoline.

(4) That substituted 1-alkyltetrahydro*iso*quinolines do not undergo this type of change.

235. "Contributions to the theory of solutions." By John Holmes and Philip John Sageman.

The authors have investigated the changes in volume which occur on mixing methyl iodide with ethyl alcohol, *n*-propyl alcohol, and acetone. The conclusion is drawn that acetone is aggregated in a similar manner to the *n*-primary alcohols, and that methyl iodide possesses twice this complexity; this conclusion receives support from the proportions of methyl iodide in admixture with the lower primary alcohols which exhibit a maximum absorption of heat. Aniline and ethyl acetate are also found to be aggregated similarly to the *n*-primary alcohols.

It is found that the change in volume produced on gradually neutralising a base with an acid is directly proportional to the quantity of salt formed.

The results of the investigation tend to the conclusion that physical forces only are operative in solution, and that theories requiring electrolytic dissociation or combination of solvent with solute are unnecessary for understanding many of the phenomena common to aqueous and non-aqueous mixtures.

236. "The constitution of polynitrophenols in alkaline solution." By Bertram Haward Buttle and John Theodore Hewitt.

The absorption spectra of 2 : 4- and 2 : 6-dinitrophenols in acid and alkaline solution have been examined, and whilst the latter gives solutions showing absorptions similar to those of *o*-nitrophenol, solutions of the 2 : 4-isomeride show more resemblance to *p*-nitrophenol. The conclusion is thus drawn that 2 : 4-dinitrophenol gives para- rather than ortho-quinonoid salts.

Picric acid, being a very strong acid, is nearly completely ionised in dilute aqueous solution, the absorption spectrum produced by an aqueous solution of the acid being practically identical with that of the sodium salt, but differs very markedly from that given by 2 : 4 : 6-trinitroanisole.

Attention was drawn to the influence exerted on nitro-groups attached to aromatic nuclei by other nitro-groups in the meta-position.

237. "The preparation of disulphides. Part VII. The nitrobenzyl mercaptans and disulphides." By Thomas Slater Price and Douglas Frank Twiss.

By the hydrolysis of the three sodium alkyl thiosulphate compounds, the corresponding *o*-, *m*-, and *p*-nitrobenzyl mercaptans have been prepared. By oxidation with iodine the corresponding disulphides were obtained. The properties of the disulphides prepared in this way agree with those of the compounds obtained by the action of alkali on the sodium nitrobenzyl thiosulphates (*Trans.*, 1908, **93**, 1402).

The method of preparation of *p*-nitrobenzyl disulphide given by Strakosch (*Ber.*, 1872, **5**, 692) was investigated and shown to yield a mixture of the monosulphide, disulphide, and mercaptan. The substance described by Strakosch as the disulphide appears to have been a mixture of the disulphide and mercaptan, and the compound described by him as the mercaptan was really the impure monosulphide.

The melting points of the nitrobenzyl mercaptans are: ortho, 29·5°; meta, 14°; and para, 52·5°. These are slightly different from those given by previous observers, the discrepancies being probably due to traces of disulphide in the mercaptans previously obtained.

Gutmann's recent results (*Ber.*, 1909, **42**, 228) on the action of acids on sodium and potassium ethyl thiosulphates were discussed, and shown to be in accordance with the usually accepted constitutional formula for sodium thiosulphate.

238. "A colorimetric method for the estimation of small quantities of vanadium." By Arnold William Gregory.

The method is based on the colour reaction which takes place when a solution of vanadium in concentrated sulphuric acid is added to a solution of strychnine in the same acid. A violet colour is first formed, and this changes to orange. As the latter colour is quite permanent, and is proportional to the quantity of vanadium present, a comparison of the colour produced with that given by a known amount of vanadium under similar conditions indicates the amount of vanadium present in the solution tested. This test is not given by titanium, tungsten, or molybdenum, nor does their presence in relatively large quantities interfere with the formation of the colour given by vanadium. The presence of iron interferes with the reaction. This element must therefore be removed before the test can be applied.

239. "**Chlorination and bromination of acylanilides. A direct process.**" (Preliminary note.) **By Kennedy Joseph Previté Orton and William Jacob Jones.**

In the chlorination (or bromination) of acylanilides, the chloroamines, $Ar{\cdot}NCl{\cdot}Ac$, are not intermediate steps, in the sense that they are first formed, and then change by an intramolecular rearrangement into the chloroacylanilides. The substitution of hydrogen in the benzene nucleus of anilides is rather the result of a direct interaction of chlorine (or bromine) and anilide. In the conversion of a chloroamine into the isomeric anilide under the influence of hydrochloric acid, the presence of which is essential, the chloroamine first reacts with hydrochloric acid, thus: $Ar{\cdot}NCl{\cdot}Ac + HCl \rightleftarrows Ar{\cdot}NH{\cdot}Ac + Cl_2$ (Orton and Jones, Trans., 1909, **95**, 1456); then the free chlorine and the anilide interact.

Among the mass of evidence which the authors have accumulated in favour of the above statement, the following will serve as an illustration. In a solution of acetylchloroamino-*p*-chlorobenzene and hydrochloric acid (concentration of each = 0·025 gram-molecules per litre) in 50 per cent. acetic acid, in which about 1·2 per cent. of the total chlorine is free, the formation of 2 : 4-dichloroacetanilide is about twice as rapid as the formation of *p*-(and *o*-)chloroacetanilide in a similar equimolecular system composed of acetylchloroaminobenzene and hydrochloric acid, in which only a trace of free chlorine is found. Yet in a system composed of acetylchloroamino-*p*-chlorobenzene, acetanilide, and hydrochloric acid in the same medium, the acetanilide only is chlorinated; *o*- and *p*-chloroacetanilides are formed, but no 2:4-dichloroacetanilide. The speed of the change is about six times that of the system composed of acetylchloroaminobenzene and hydrochloric acid. On the assumption that the formation of the monochloroacetanilides is from the chlorine (set free from the acetylchloroamino-*p*-chlorobenzene) and acetanilide and not through the chloroamine of acetanilide, it should follow, since no 2 : 4-dichloroacetanilide is produced, that the rate of interaction of chlorine and acetanilide is very large relative to that of chlorine and *p*-chloroacetanilide. Comparative measurements made in glacial acetic acid, where only chlorine and anilide but no chloroamine are present (*loc. cit.*), show that the chlorination of acetanilide is about 160 times as speedy as that of *p*-chloroacetanilide.

From this view of the process of chlorination, it follows that the velocity is given by $k \cdot c^{(\text{anilide})} \cdot c^{(\text{chlorine})}$; but since the equilibrium $c^{(\text{chloroamine})} \cdot c^{2\,(\text{hydrochloric acid})} = K \cdot c^{(\text{anilide})} \cdot c^{(\text{chloride})}$ holds (Orton and Jones, *loc. cit.*), the velocity equals $k \cdot c^{(\text{chloroamine})} \cdot c^{2\,(\text{hydrochloric acid})}/K$. Since the concentration of hydrochloric acid remains constant during the con-

version of the chloroamine into a chloroanilide, the velocity of conversion in a system in which the proportion of chlorine and anilide is small (dilute acetic acid) is proportional to the original concentration (C) of the chloroamine, and $= k \,.\, C^{(\text{chloroamine})}$. Const./$K$; that is, the reaction is apparently unimolecular. When the proportion of chlorine and anilide is small, and at the same time the hydrochloric acid, the concentration of which is varied, is in excess, the speed of the transformation is approximately proportional to the square of the concentration of the hydrochloric acid used in the system. In Blanksma's observations on the transformation of acetylchloroaminobenzene, in which a considerable excess of hydrochloric acid was used, the reaction was found to be apparently unimolecular, and the speed proportional to the square of the concentration of the hydrochloric acid. When the above limitations are not imposed, the present measurements show that the reaction is not apparently unimolecular and the speed is not approximately proportional to the square of the concentration of the hydrochloric acid, but is in accord with the proposition laid down in the foregoing.

When chlorine and an anilide interact, two changes occur, namely, the formation of a C-chloro-derivative, an irreversible change, and the formation of an N-chloro-derivative, a reversible change. With the great majority of anilides, when the acetic acid medium is sufficiently dilute, the latter reaction is the more rapid; the equilibrium above mentioned is attained, which is only slowly displaced by the formation of the C-chloro-derivative. In the case of acetanilide, however, chlorination in the nucleus is faster than in the imino-group.

It is suggested that the peculiar influences of amino-, imino-, and hydroxy-groups on substitution in the benzene nucleus are largely due to the possibility which their presence offers of the transient formation of highly reactive o- and p-quinonoid phases of the benzene nucleus.

240. "The benzyl and nitrobenzyl selenosulphates and the benzyl and nitrobenzyl diselenides." By Thomas Slater Price and Lionel Manfred Jones.

In a preliminary note (Proc., 1908, **24**, 134) the preparation of benzyl diselenide from sodium selenosulphate and benzyl chloride has been described. An attempt to extend this method of preparation to the nitrobenzyl diselenides was not successful until the sodium selenosulphate was replaced by the potassium salt.

The diselenides were prepared from the alkyl selenosulphates either by the action of iodine or by electrolysis in a divided cell after potassium hydrogen carbonate had been added to the solution

(compare Price and Twiss, *Trans.*, 1907, **91**, 2021). The iodine method was the most general one, the reaction taking place quantitatively at the ordinary temperature, according to the equation:

$$2KO{\cdot}SO_2SeR + 2H_2O + I_2 = R_2Se_2 + 2KHSO_4 + 2HI.$$

This reaction was made use of in the analysis of the selenosulphates. Benzyl and also the *p*- and *m*-nitrobenzyl diselenides could be prepared by the electrolytic method, but not the corresponding ortho-compound.

The potassium benzyl and nitrobenzyl selenosulphates are all crystalline compounds, which are fairly readily soluble in water; the solutions give no precipitate with barium chloride. The *p*-nitrobenzyl compound possesses a slight creamy tinge, the others being colourless.

The diselenides are all more or less yellow, crystalline compounds, their melting points being: benzyl, 92—93°; nitrobenzyl: ortho, 103·5°; meta, 106°; para, 107·5°.

Both the selenosulphates and the diselenides undergo decomposition with liberation of selenium on exposure to diffused daylight. The benzyl compounds are the least stable, turning red in a few hours. Exposure of one or more days is necessary to affect the nitrobenzyl compounds, the meta being the most stable.

241. "**The action of ammonia on the glycide aryl ethers. Part I. *o*-Tolyloxypropanolamines.**" **By David Runciman Boyd and [in part] Herbert S. Knowlton.**

Glycide o-tolyl ether, $O<\begin{matrix}CH{\cdot}CH_2{\cdot}O{\cdot}C_7H_7\\ |\\ CH_2\end{matrix}$, an oil boiling at 134·5°/14 mm., has been prepared, and the action of aqueous ammonia on it has been investigated.

Three bases have been isolated, namely, *β-amino-β'-o-tolyloxyisopropyl alcohol*, $C_{10}H_{13}O_2{\cdot}NH_2$, m. p. 58—60°, b. p. 177°/11 mm.; *dihydroxy-di-o-tolyloxydipropylamine*, $(C_{10}H_{13}O_2)_2NH$, m. p. 117·5°, and *trihydroxy-tri-o-tolyloxytripropylamine*, $(C_{10}H_{13}O_2)_3N$, m. p. 83—84°.

Various derivatives of these bases were described.

242. "**The action of potassium hydroxide on epichlorohydrin in presence of monohydric phenols.**" **By David Runciman Boyd and Ernest Robert Marle.**

A criticism of Zunino's paper (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 254).

The following new compounds were described: *glycerol dithymyl ether*, $OH{\cdot}CH(CH_2{\cdot}O{\cdot}C_{10}H_{13})_2$, m. p. 41·5—42°, b. p. 270°/28 mm., and *glycide thymyl ether*, $O<\begin{matrix}CH{\cdot}CH{\cdot}O{\cdot}C_{10}H_{13}\\ |\\ CH_2\end{matrix}$, b. p. 158°/16 mm.

243. "Reactivity of the halogens in organic compounds. Part III. Interaction of bromoacetic, α-bromopropionic, and α-bromobutyric acids and their sodium salts with water and with alkali." By George Senter.

The results of the velocity measurements are summarised in the accompanying table, in which k in each case represents the initial velocity, in $N/10$-solution at 52·4°, of the reaction represented by the equation below which it is placed. The numbers in brackets give the relative initial velocities of the reactions under equivalent conditions, referred to the slowest—the reaction between bromoacetic acid and water—as unity.

$CH_2Br\cdot CO_2H + H_2O$.	$CHMeBr\cdot CO_2H + H_2O$.	$CHEtBr\cdot CO_2H + H_2O$.
$k = 0{\cdot}000085$	0·00017	0·00022
[1]	[2]	[2·6]
$CH_2Br\cdot CO_2Na + H_2O$.	$CHMeBr\cdot CO_2Na + H_2O$.	$CHEtBr\cdot CO_2Na + H_2O$.
$k = 0{\cdot}00010$	0·0014	0·0026
[1·2]	[16]	[30]
$CH_2Br\cdot CO_2Na + NaOH$.	$CHMeBr\cdot CO_2Na + NaOH$.	$CHEtBr\cdot CO_2Na + NaOH$.
$k = 0{\cdot}0065$	0·0009	0·0007
[76]	[9]	[8]
$CH_2Br\cdot CO_2H + AgNO_3$.	$CHMeBr\cdot CO_2H + AgNO_3$.	$CHEtBr\cdot CO_2H + AgNO_3$.
$k = 0{\cdot}0064$	0·48	1·44
[76]	[5700]	[17000]

As regards the mechanism of the chemical changes, the main reaction for those of the first type probably takes place between non-ionised acid and non-ionised water. In the case of the sodium salts and water, the experimental results are best accounted for on the assumption that the anion loses a bromine atom along with the negative electron, thus: $R\cdot CHBr\cdot COO' \longrightarrow R\cdot CH\cdot COO + Br'$, the residue immediately uniting with water to form the hydroxy-acid. The main reaction with the sodium salts and sodium hydroxide takes place between the anions $R\cdot CHBr\cdot COO'$ (where R represents hydrogen or an alkyl group) and OH' ions. The comparatively slow reaction between these ions (as contrasted with the rapidity of ester hydrolysis) is probably due to repulsion between the negative charges on the two groups. The results with silver nitrate are provisional, and these reactions will be discussed in a later communication.

244. "Ethyl ether. Part I. The influence of water and alcohol on its boiling-point." By John Wade and Horace Finnemore.

Ether as usually purified is not homogeneous, and is resolvable into two physical constituents by accurate fractionation. The more volatile constituent contains water that has escaped the ordinary

drying agents, and under suitable conditions may be isolated as a binary mixture of ether and water, having a constant and minimum boiling-point, 34·15° (corr.), and containing about 1·3 per cent. of water. At the ordinary temperature this binary mixture is practically a saturated solution of water in ether; it has been found incidentally that the solubility of water is approximately constant at 0·013 gram per gram of ether between 20° and 15°, and then decreases to 0·009 gram per gram at 10°, the lowest temperature examined.

The less volatile constituent obtained on fractionating ordinary ether is approximately pure ether, b. p. 34·50° (corr.). In presence of alcohol the boiling point may be appreciably raised, by an amount varying with the proportion of alcohol in the still; the highest observed was 34·73° (corr.). There is no evidence, however, of the formation of a definite physical mixture, for although a very appreciable amount of alcohol passes over with the ether, this may be gradually eliminated by repeated fractionation. Alcohol has a similar influence on the boiling point of the binary aqueous mixture, and when ether containing both water and alcohol is fractionated, indications of a third physical constituent are sometimes obtained. This, however, is not due to the formation of a binary mixture of ether and alcohol, nor to that of a ternary mixture of all three substances, but is probably caused by the elevation in the boiling point of the binary aqueous mixture as the concentration of the alcohol increases.

The mutually opposing influences of water and alcohol on the boiling point of ether render constancy of its boiling point as determined in the ordinary manner useless as a criterion of purity.

245. "A method for the measurement of vapour pressures." By Alexander Charles Cumming.

A solution or hydrate is kept at constant temperature in an evacuated glass vessel, and the vapour tension measured by a dew-point method. In the apparatus described, a silver cylinder is cooled slowly and the temperature noted at which dew appears on the silver surface. The corresponding vapour pressure is then obtained by reference to a table of vapour pressures of the pure solvent. With attention to certain details, the method was found to be convenient and accurate. The vapour pressures of different concentrations of sulphuric acid at various temperatures were determined, and the results were found to be in good accord with the values given by Regnault and by Sorel. A few measurements of the vapour tensions of salt hydrates were also made. The method has the marked advantage over the differential tensimeter method that no error is introduced by small amounts of residual air in the apparatus.

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RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, 6th December, 1909.

All persons who received grants in December, 1908, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Wednesday, 1st December.

The Council wish to draw attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal tar and allied industries.

At the next Ordinary Scientific Meeting on **Thursday**, November **4th**, 1909, at **8.30** p.m., the following papers will be communicated:

"Dynamics of the reaction between iodine and acetone." By H. M. Dawson and Miss M. S. Leslie.

"The formation and reactions of imino-compounds. Part XI. The formation of 1-imino-2-cyano*cyclo*pentane from adiponitrile." By J. F. Thorpe.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 12/11/09.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 361.

Thursday, November 4th, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

Messrs. R. Müller and H. S. Wills were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Arthur Fordshaw, M.Sc., 104, Holly Road, Handsworth, Birmingham.

Alexander David Gardiner, 6, Wellfield Terrace, Springburn, Glasgow.

Eric John Holmyard, 7, Manor Street, Cambridge.

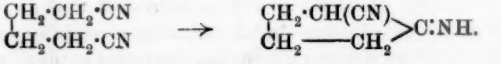
Francis Hugh Ping, 10, Forest Place, Whipps Cross Road, Leytonstone, N.E.

Richard Vernon Wheeler, D.Sc., British Coal Dust Experiments Committee, Altofts Colliery, Normanton.

Of the following papers, those marked * were read:

*246. "The formation and reactions of imino-compounds. Part XI. The formation of 1-imino-2-cyano*cyclo*pentane from adiponitrile.' By Jocelyn Field Thorpe.

A method was described by which αδ-dicyanobutane (adiponitrile) can be completely converted into 1-imino-2-cyano*cyclo*pentane in accordance with the scheme:



DISCUSSION.

The PRESIDENT asked whether, if the second cyano-group was necessary for the reaction to proceed (though it remains at the end

unchanged), it did not point to a transitory interaction between this group and the catalyst?

Dr. J. F. THORPE, in reply, said that the precise mechanism of the reaction was still open to question, but the nitrile group remaining unaffected apparently had some influence, since its presence seemed to be essential.

In reply to Dr. MORGAN, he stated that the use of piperidine, diethylamine, and other catalytic agents of that type did not lead to the formation of imino-compounds.

In reply to Mr. BALY, Dr. Thorpe said that so far as he knew there was no chemical evidence of a hydrogen atom of the methylene group of ethyl cyanoacetate wandering to the nitrogen atom under the influence of sodium ethoxide.

***247. "Studies in the camphane series. Part XXVII. Camphoryl-phenyltriazen (camphordiazoaminobenzene) and its bearing on the constitution of diazoamino-compounds." By Martin Onslow Forster and Charles Samuel Garland.**

From a study of the compounds derived from aminocamphor and from methylaminocamphor by coupling these bases with diazonium salts, the authors conclude that aliphatic-aromatic diazoamino-compounds must be represented by the expression $X{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5$, the hydrogen atom of the triazen nucleus taking up a position of superior stability in the neighbourhood of the phenyl group rather than that of the alkyl radicle, X.

DISCUSSION.

Dr. MORGAN said that the authors' experiments amply justified the conclusions which they deduced in regard to the constitution of mixed aliphatic-aromatic diazoamines.

With reference to mixed diazoamines containing two aryl (benzenoid) groups X and Y, he could not, in the present state of knowledge, share Dr. Forster's belief that the coupled product of diazonium salt, $X{\cdot}N_2Cl$, and aromatic amine, $Y{\cdot}NH_2$, is entirely either $X{\cdot}N_2{\cdot}NH{\cdot}Y$ or

$$X{\cdot}NH{\cdot}N_2{\cdot}Y.$$

He preferred to regard the product, formed under the ordinary experimental conditions, as a mixture of these two isomeric diazoamines.

The observations of Griess, Meldola, Schraube, Hantzsch, and others showed conclusively that, when a diazonium salt and an aromatic amine are dissolved together in dilute acid, a certain amount of rearrangement occurs consequent on the migration of diazo-nitrogen. The solution, if only feebly acid, then contains the following four reagents, *a*, *b*, *c*, and *d* (two diazo-hydroxides and two primary aromatic amines), produced by hydrolysis from their respective salts.

$$\begin{array}{ccc} X\cdot N_2\cdot OH & & Y\cdot NH_2 \\ & a \longleftrightarrow b & \\ X\cdot NH_2 & & Y\cdot N_2\cdot OH \\ & c \longleftrightarrow d & \end{array} \longrightarrow \left\{ \begin{array}{l} X\cdot N_2\cdot NH\cdot Y \\ X\cdot NH\cdot N_2\cdot Y \end{array} \right\}.$$

In the formation of the mixed diazoamine, coupling occurs along the lines *ab* and *cd*, with the result that the precipitated product is a mixture in which the proportions of $X\cdot N_2\cdot NH\cdot Y$ and $X\cdot NH\cdot N_2\cdot Y$ depend on the extent to which the migration of diazo-nitrogen has occurred.

The same result is obtained whether one starts with $X\cdot N_2Cl$ and $Y\cdot NH_2$ or with $Y\cdot N_2Cl$ and $X\cdot NH_2$. Migration of diazo-nitrogen occurs in either case; the same four reagents, *a*, *b*, *c*, and *d*, become effective, and their interaction determines the nature of the coupled product.

Dr. J. F. Thorpe pointed out that if the system of three nitrogen atoms with a double valency between two of them described by Dr. Forster could be considered as analogous to the system of two carbon atoms and one oxygen atom (C·C:O), as in ethyl acetoacetate, or to the system of three carbon atoms with a double valency between two of them (C·C:C), as in glutaconic acid, then any hydrogen attached to the extreme nitrogen atoms might be regarded for experimental purposes as being attached to the central nitrogen atom, thus:

in the same manner as in glutaconic acid.

In no case of this kind would there be reasonable hope of obtaining any trustworthy chemical evidence respecting the position of the hydrogen atom.

Dr. Forster was prepared to admit that aromatic diazoamino-compounds, when produced in the coupling process, exposed to light, and recrystallised from hot solvents, behaved as Dr. Morgan indicated, namely, as a mixture of two isomeric diazoamines, but he attributed this to an alteration of $X\cdot N_2\cdot NH\cdot Y$ into $X\cdot NH\cdot N_2\cdot Y$, effected by the environment, such alteration proceeding with greater facility when the attraction exerted by Y for the hydrogen in the triazen chain did not differ greatly from that exerted by X. He was led to this conclusion principally by three circumstances.

1. The numerous cases of resolution by acids upon which current views regarding the constitution of aromatic diazoamino-compounds are based have been studied most frequently at temperatures ranging from that of the laboratory to 100°, instead of at zero or below.

2. When prepared by Dimroth's method, from arylazoimide and magnesium aryl halide, α-naphthylphenyltriazen is resolved by

alcoholic hydrogen chloride below zero into α-naphthyldiazonium chloride and aniline, unaccompanied by α-naphthylamine.

3. There does not appear to have been recorded a case in which two isomeric diazo-carbamides have arisen by direct action of phenylcarbimide on a diaryltriazen.

248. "Dynamics of the reaction between iodine and acetone." By Harry Medforth Dawson and May Sybil Leslie.

The physical properties of solutions of iodine in acetone are abnormal, and it has been found that this is due to a reaction resulting in the formation of hydrogen iodide and one or more iodoacetones. At the ordinary temperature the reaction takes place fairly rapidly, but is incomplete, indicating that the change is reversible.

In order to elucidate its mechanism, the authors have made measurements of the velocity of the reaction, the rate of change being diminished by dissolving the reacting substances in various inert solvents. In aqueous solution, the reaction proceeds much more nearly towards completion than it does in carbon tetrachloride, benzene, nitrobenzene, methyl alcohol, or methyl acetate. On the other hand, the velocity of the change in neutral solution appears to be much slower in water than it is in the other solvents used.

A detailed examination of the reaction in aqueous solution has shown that in presence of acids the rate of disappearance of the iodine is constant when the acetone is present in relatively large excess. In solutions acidified with sulphuric acid, the velocity is proportional to the concentration of the acid and also to that of the acetone. If no foreign acid is added, an autocatalytic effect is observed, due to the hydrogen iodide formed during the reaction.

249. "Studies in phototropy and thermotropy. Part I. Arylidene- and naphthylidene-amines." By Alfred Senier and Frederick George Shepheard.

In a recent paper, the authors described a series of Schiff's bases (salicylidene-amines), one of which, namely, salicylidene-*m*-toluidine, was found to be highly phototropic (*Trans.*, 1909, **95**, 441). The investigation has now been extended to the study of a number of other salicylidene-amines and related compounds, and five compounds, including salicylidene-*m*-toluidine, which exhibit phototropy have been prepared.

Early in this investigation it was observed that many of the coloured bases became deeper in colour on heating, and that this change, like phototropy, was reversible. The whole of the compounds in question were then subjected to an examination to obtain further

evidence, if possible, of this property. Their colour changes were noted (1) between the ordinary temperature and a temperature just below their melting points, and (2) between the ordinary temperature and that of solid carbon dioxide. This led to the interesting fact that most of the compounds exhibit this phenomenon, which has long been known, in isolated instances, among inorganic substances. This reversible change of colour the authors propose to term *thermotropy*.

Whilst it is possible that phototropic and thermotropic isomerism may be explained by intramolecular rearrangement, as is generally supposed, it seems more probable, bearing in mind that the substances affected are solids, that it depends on different modes of aggregation of the ordinary molecules which may be supposed to be grouped together in the probably much more complex molecules of solids.

250. "**The action of mercaptans on acid chlorides. Part I. Oxalyl chloride; the mono- and di-thio-oxalates.**" By **Humphrey Owen Jones and Hubert Sanderson Tasker.**

The following esters of dithio-oxalic acid have been prepared by the action of oxalyl chloride on the corresponding mercaptans or their metallic derivatives. *Phenyl dithio-oxalate*, a sulphur-yellow solid, melting at 119—120°, and distilling undecomposed. *Methyl dithio-oxalate*, pale yellow prisms, melting at 82·5—83·5°. *Ethyl dithio-oxalate*, yellow prisms, melting at 27—27·5°, and distilling at 235°. *Propyl dithio-oxalate* and *amyl dithio-oxalate*, yellow liquids, the former distilling at 158°/15 mm., and the latter at 206°/19 mm.

On boiling these esters with an alcoholic solution of potassium hydrosulphide, the mercaptan is set free, and *potassium dithio-oxalate*, $(KSCO)_2$, separates as a white, crystalline powder. This salt can be used as a delicate test for nickel or cobalt, owing to the formation of a complex potassium nickelo- or cobalto-thio-oxalate, which is intensely coloured. The nickel salt is less stable towards potassium cyanide and strong acids than the cobalt salt, so that by adding potassium cyanide the colour of the nickel salt can be destroyed before that of the cobalt salt, and in this way 10 per cent. of cobalt can be detected in the presence of 90 per cent. of nickel. The colour of the nickel and cobalt salts can be seen readily at dilutions of 1 in 40,000,000 on looking through 25 cm. of solution.

251. "**The action of mercaptans on acid chlorides. Part II. The acid chlorides of phosphorus, sulphur, and nitrogen.**" By **Hubert Sanderson Tasker and Humphrey Owen Jones.**

Phosphorus trichloride reacts with phenyl mercaptan or its metallic derivatives to give triphenyl trithiophosphite as stated by Schwarze;

phosphoryl chloride similarly gives triphenyl trithiophosphate, melting at 115° (Schwarze gave the melting point as 72°, and this was corrected by Michaelis).

Sulphuryl chloride in the cold gives a deep yellow colour, probably due to the formation of an ester, which disappears with the formation of phenyl disulphide and the evolution of sulphur dioxide.

Thionyl chloride also gives a yellow colour in the cold, but this again disappears quickly; phenyl disulphide is formed and sulphur dioxide is evolved, but the possible new oxide of sulphur, SO, is not formed.

Numerous experiments were made to discriminate between the two following equations to represent this reaction :

$$8C_6H_5\cdot SH + 4SOCl_2 = 8HCl + 2SO_2 + 3(C_6H_5\cdot S)_2 + (C_6H_5)_2S_4$$
$$4C_6H_5\cdot SH + SOCl_2 = (C_6H_5\cdot S)_2 + (C_6H_5)_2S_3 + H_2O + 2HCl.$$

It was found that both reactions seem to take place simultaneously, but that the main reaction appears to be represented by the first equation.

Nitrosyl chloride reacts readily with mercaptans in the cold; hydrogen chloride is evolved, and brilliant red colours are produced (probably due to the formation of esters of thionitrous acid), which gradually disappear with the evolution of nitric oxide and the formation of alkyl disulphide. The same colour is produced by the action of the chloride on the mercaptides. When nitrosyl chloride is treated with an alkyl mercaptan at a low temperature (solid carbon dioxide and ether), a small quantity of hydroxylamine hydrochloride is always formed.

252. "The colouring matters of the flowers of Hibiscus sabdariffa and Thespasia lampas." By Arthur George Perkin.

The flowers of the *Hibiscus sabdariffa* yielded 0·36 per cent. of a mixture of three yellow colouring matters, the main constituent of which, $C_{15}H_{10}O_8$, crystallising in yellow needles, gives an *acetyl* derivative, $C_{15}H_4O_8(C_2H_3O)_6$, m. p. 229—230°, and, on fusion with alkali, protocatechuic acid. It was identical with gossypetin present in Indian cotton flowers (*Gossypium herbaceum*), the formula, $C_{16}H_{12}O_8$, previously given for which is now abandoned. Together with quercetin, the flowers yielded a trace of a sparingly soluble new colouring matter, for which the name *hibiscetin* is proposed; this melts at about 340°, and gave a colourless *acetyl* compound, m. p. 238—239°. In addition to these substances, free protocatechuic acid was also isolated. The flowers of *Thespasia lampas* gave quercetin to the extent of 0·6 per cent., together with a small quantity of free protocatechuic acid.

253. "**The reduction of 4-hydroxy-*o*-toluic acid.**" **By Oscar Baudisch, Gilbert Stanley Hibbert, and William Henry Perkin, jun.**

By reducing 4-hydroxy-*o*-toluic acid with sodium and alcohol, the authors have obtained the four possible isomerides, namely, the two cis- and the two trans-1-*methyl*cyclo*hexan*-4-*ol*-2-*carboxylic acids*, of which various derivatives were described. 1-*Methyl*-Δ^6-cyclo*hexen*-4-*ol*-2-*carboxylic acid* is also formed in this reaction.

254. "**The reduction of 6-hydroxy-*o*-toluic acid.**" **By Oscar Baudisch and William Henry Perkin, jun.**

On reduction with sodium and alcohol, 6-hydroxy-*o*-toluic acid yields a mixture of cis- and trans-1-*methyl*cyclo*hexan*-6-*ol*-2-*carboxylic acid*.

255. "**The reduction 5-hydroxy-*m*-toluic acid.**" **By Andrew Norman Meldrum and William Henry Perkin, jun.**

By reducing 5-hydroxy-*m*-toluic acid with sodium and *iso*amyl alcohol, the authors have prepared trans-1-*methyl*cyclo*hexan*-5-*ol*-3-*carboxylic acid*. This is converted into the corresponding cis-*acid* by distillation and hydrolysing the resulting lactone.

256. "**The reaction between potassium permanganate and manganese sulphate in acid solution.**" **By Anukul Chandra Sirkar and Jatindra Mohon Dutta.**

The authors find that in neutral or very faintly acid solution at 85° the reaction between potassium permanganate and manganese sulphate is in accordance with the equation:

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

In solution freely acidified with sulphuric acid at 85° the reaction is practically the same as in neutral or faintly acid solution; at 100° the manganese dioxide which has been formed by the interaction between the permanganate and manganese salt is attacked by the acid of the solution, forming a certain quantity of manganese sulphate in accordance with the equation:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

The manganese sulphate thus formed reacts with a further quantity of potassium permanganate,

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4,$$

and these two reactions occur in a cycle indefinitely, or so long as the solution remains freely acid.

In solutions which were at the start neutral, a certain amount of sulphuric acid is at first produced, but this subsequently becomes used up, and thus in this case a limit is put to the amount of permanganate reduced by a limited quantity of manganese salt even at 100°.

This investigation offers an explanation of what might be termed the catalytic reduction of potassium permanganate in freely acid solution by either manganese salt or manganese dioxide.

257. "The condensation of ketones and aldehydes with the sodium derivative of ethyl cyanoacetate. Part II." By Henry Dent Gardner, jun., and Walter Norman Haworth.

An account was given of the investigation of the products formed by the condensation of ethyl sodiocyanoacetate with acetone, methyl ethyl ketone, methyl propyl ketone, diethyl ketone, and methyl hexyl ketone.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, 6th December, 1909.

All persons who received grants in December, 1908, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Wednesday, 1st December.

The Council wish to draw attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal tar and allied industries.

ERRATA.

1909. P. 187, line 8, *for* "formally elected" *read* "formally admitted."

P. 213, line 13, *for* "$16\overline{\mathrm{H}}+2$" *read* "$16\overline{\mathrm{H}}+2\mu$."

At the next Ordinary Scientific Meeting on **Thursday**, November **18th**, 1909, at **8.30** p.m., the following papers will be communicated:

"The resolution of asymmetrical derivatives of phosphoric acid." By B. D. W. Luff and F. S. Kipping.

"The configuration of tropeine and γ-tropeine and the resolution of atropine." By M. Barrowcliff and F. Tutin.

"The electromotive behaviour of cuprous oxide and cupric hydroxide in alkaline electrolytes." By A. J. Allmand.

"Note on the stereoisomeric modifications of $a\beta$-dibromobenzylacetone." By Miss I. Smedley.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

[*Issued* 29/11/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. No. 362.

Thursday, November 18th, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

It was announced from the Chair that, on the motion of the PRESIDENT, seconded by Dr. Hugo Müller, the Council of the Society had, that afternoon, unanimously passed the following resolution :— The Council of the Chemical Society have heard with deep regret of the death of Dr. W. J. Russell, F.R.S., Past President of the Society. The Council recall the long services of Dr. Russell to the Society extending over nearly half a century. Elected a Fellow of this Society in 1851, Dr. Russell was first chosen a member of the Council in 1863, and with one short interval he served the Society continuously until his death. He was Vice-President in 1872, Secretary from 1873 to 1875, Treasurer from 1875 to 1889, and President from 1889 to 1891. Dr. Russell's communications to the Society began in the year 1855. Chemists throughout the world recognise the scientific importance of his memoirs on the atomic weights of Nickel and Cobalt, on the Absorption Spectra of solutions, and on the action of metals and of wood on photographic plates; and all workers on gas analysis are indebted to Dr. Russell for the new methods and apparatus he designed for the manipulation and measurement of gases. On behalf of the Chemical Society the Council desire to express their sense of the great loss that the Society and British Science have sustained, and beg to convey to the relatives of Dr. Russell their sincerest sympathy.

Signed, on behalf of the Society,
HAROLD B. DIXON,
President.

It was stated from the Chair that the Society had become indebted to Professor Meldola, F.R.S., for an interesting photograph of the Paris Exhibition Jury, 1900.

Certificates were read for the first time in favour of Messrs.:

Arthur Jaques, B.Sc., 23, St. Oswin's Avenue, Cullercoats, Northumberland.

Samuel Judd Lewis, B.Sc., Ph.D., 122, Newington Causeway, S.E.

Herbert William Southgate, B.Sc., 130, Horseferry Road, Westminster, S.W.

Stuart Jardine Norris Wolfenden, The Grange, Sidcup, Kent.

Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (3) in favour of Messrs.:

Edmund Victor Flack, Mayville, Wigtown Road, Green Point, S. Africa.

John Muller, B.A., Government Analytical Laboratory, Grahamstown, Cape Colony.

Joas Cornelio Rodrigues Peixoto, 52, Rua N.S. Copacabana, Rio de Janeiro (Brazil).

Charles Tapp, Cradock, Cape of Good Hope.

Joseph Pretty Wright, 883, Burrard Street, Vancouver, B.C.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON,
LONDON, S.W.
November 17th, 1909.

GENTLEMEN,

I beg to present to the Council of the Chemical Society the Report of the International Committee on Atomic Weights, 1910, to which I have affixed, as desired by them, the signatures of Professors Ostwald and Urbain.

Since the Committee last reported, new determinations have been made of the atomic weights of chlorine, nitrogen, carbon, iodine, silver, phosphorus, arsenic, chromium, tellurium, mercury, palladium, krypton, and xenon.

Certain of the numbers obtained, if confirmed, would necessitate minor alterations in the tables, but as additional determinations are promised we prefer to make no very great changes until corroborative

evidence is forthcoming. We suggest, however, that the value of Cr should be 52·0; that of As should be changed to 74·96; and we adopt the new values for krypton and xenon.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee of Atomic Weights, 1910.

Since the preparation of our last report there has been much activity in the determination of atomic weights. A brief summary of the results obtained is as follows:

Chlorine.—A novel comparison of chlorine with oxygen is due to Guye and Fluss (*J. Chim. Phys.*, 1908, **6**, 732). Nitrosyl chloride, NOCl, was first weighed, and then distilled over silver to absorb chlorine, then over heated copper to absorb oxygen, and finally over metallic calcium, which retained the nitrogen. The complete analysis of the chloride was thus effected. From the direct weights of the oxygen and chlorine, Cl = 35·468.

Nitrogen.—In the investigation just cited, Guye and Fluss give data which correspond to N = 14·006. Guye and Pintza (*Compt. rend.*, 1908, **147**, 925) determined the density of the mixed gases produced by the decomposition of ammonia, and so measured its composition by volume. If H = 1·0076, then N = 14·014. The authors regard the determination as having only a significance corroborative of the lower value for nitrogen.

The ratio $AgCl : NH_4Cl :: 100 : 37·3217$ has been measured by Richards, Koethner, and Tiede (*J. Amer. Chem. Soc.*, 1909, **31**, 6). Reduced with Ag = 107·881, Cl = 35·4574, and H = 1·0076, N = 14·0085. If H = 1·0078, N = 14·008. The values assigned to silver and chlorine are derived from former researches by Richards and his colleagues in the Harvard laboratory.

Carbon.—From the ratio between silver and tetraethylammonium bromide, as measured by Scott (*Trans.*, 1909, **95**, 1200), C = 12·017 when Ag = 107·88. A single experiment with the corresponding methyl compound gave C = 12·019. These values are too high to be accepted until they have been confirmed by other methods.

From the density of methane, Baume and Perrot (*Compt. rend.*, 1909, **148**, 39) find C = 12·004. From the density of toluene, as

determined by Ramsay and Steele, Leduc (*Compt. rend.*, 1909, **148**, 832) computes C = 12·003.

Iodine and Silver.—Baxter and Tilley (*J. Amer. Chem. Soc.*, 1909, **31**, 201) have determined the ratio between iodine pentoxide and silver. The pentoxide was reduced by means of hydrazine, and the hydriodic acid so produced was balanced in the usual way against silver. From the ratio thus found, $I_2O_5 :: 2Ag :: 100 : 64·6225$ and 64·6230 (two series), combined with the ratio $I : Ag :: 100 : 84·8843$, the authors find that the atomic weight of Ag lies between 107·847 and 107·850. The corresponding value for iodine is I = 126·891.

Phosphorus.—From the density of phosphine, PH_3, Ter Gazarian (*Compt. rend.*, 1909, **148**, 1397) finds P = 30·906.

Arsenic.—Atomic weight redetermined by Baxter and Coffin (*J. Amer. Chem. Soc.*, 1909, **31**, 297). The ratios $Ag_3AsO_4 : 3AgCl$ and $Ag_3AsO_4 : 3AgBr$ were determined by two methods, one by solution and precipitation in the usual way, the other by heating the arsenate in a stream of hydrochloric or hydrobromic acid. The final mean result is As = 74·957 when Ag = 107·880.

Chromium.—From analyses of silver chromate by two methods, Baxter, Mueller, and Hines (*J. Amer. Chem. Soc.*, 1909, **31**, 529) find Cr = 52·008 when Ag = 107·88. With similar analyses of silver dichromate, Baxter and Jesse (*J. Amer. Chem. Soc.*, 1909, **31**, 541) find Cr = 52·013. The mean value is 52·01.

Tellurium.—Lenher (*J. Amer. Chem. Soc.*, 1909, **31**, 20) converted the double bromide K_2TeBr_6 into 2KCl by heating, first in a stream of chlorine, and afterwards in hydrochloric acid. Sixteen very concordant experiments were made, giving the molecular ratio between the two compounds. The final mean value is Te = 127·55.

Mercury.—Analyses of mercuric chloride have been made by Easley,* who determined the proportion of mercury in the compound, and also the ratio $HgCl_2 : 2AgCl$. By the first method, Hg = 200·48; by the second method, Hg = 200·62. These values are surprisingly high; but as Easley is to continue his investigation, it would be unwise to accept them until his work is all done. It is quite possible that the increase may be ultimately verified.

Palladium.—Atomic weight determined by Gutbier, Haas, and Gebhardt† by analyses of palladosammine bromide. The final most probable mean value when $N_2H_6Br_2 = 193·908$ is Pd = 106·689.

Krypton and Xenon.—Moore (*Trans.*, 1908, **93**, 2181) isolated krypton and xenon in considerable quantities from the residues from

* *Private communication.* Easley's work is soon to be published.

† *J. pr. Chem.*, 1909, [ii], **79**, 457. This includes the work of Haas, cited in the Report for 1909.

1910.

International Atomic Weights.

		O=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	83·0
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	7·00
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·0
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·0
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·62
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·42
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	130·7
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Y	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

120 tons of liquid air. Calculated from the densities of the two gases, the atomic weights are Kr = 83·012 and Xe = 130·70.

It will be seen from the evidence given above that few changes are needed in the table of atomic weights. Chromium, 52·01, may be rounded off to 52, as compared with the 52·1 formerly accepted. Arsenic becomes 74·96, in accordance with the work of Baxter and Coffin. The new values for krypton and xenon should also be adopted. As regards mercury, action may be deferred until more evidence is received.

F. W. Clarke.
W. Ostwald.
T. E. Thorpe.
G. Urbain.

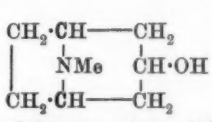
Of the following papers, those marked * were read:

***258. "The resolution of asymmetrical derivatives of phosphoric acid." By Bernard Dunstan Wilkinson Luff and Frederic Stanley Kipping.**

A full account was given of the experiments which were briefly described in a preliminary note (this vol., 203).

***259. "The configuration of tropine and ψ-tropine, and the resolution of atropine." By Marmaduke Barrowcliff and Frank Tutin.**

Tropine and ψ-tropine both possess a structure indicated by the following formula:



It was considered by Willstätter (*Ber.*, 1900, **33**, 1170) that the difference between these two bases is dependent on the relative positions in space of the hydroxyl and methyl groups.

In view of the fact that the tropine molecule contains two similar asymmetric carbon atoms (shown in heavy type), and could therefore exist in a racemic and an internally compensated form, it was thought that Willstätter's explanation should not be accepted unreservedly without further investigation. Experiments have therefore been conducted on the resolution of tropine and ψ-tropine by fractionally crystallising their salts with certain optically active acids, and it has been shown that both bases are internally compensated, thus confirming the view held by Willstätter regarding their relationship.

Atropine has been resolved by means of its d-*camphorsulphonate*, and salts of both the stereoisomeric hyoscyamines have been isolated in a state of purity. It has been shown that the latter bases, when in the form of their pure salts, have $[\alpha]_D \pm 32{\cdot}1°$, a value considerably higher than has previously been observed for hyoscyamine.

The following new salts were described: *Tropine* d-*camphorsulphonate* (m. p. 236°), *benzoyltropeine* d-*camphorsulphonate* (m. p. 240°), *ψ-tropine* d-*camphorsulphonate* (m. p. 224—226°) and d-*bromocamphorsulphonate* (m. p. 180°), *benzoyl-ψ-tropeine* d-*camphorsulphonate* (m. p. 176—177°) and d-*bromocamphorsulphonate* (m. p. 190°), d- and l-*hyoscyamine* d-*camphorsulphonates* (m. p. 135° and 159° respectively), d-*hyoscyamine auribromide* (m. p. 160°) and *picrate* (m. p. 163°).

Discussion.

Dr. Lowry inquired whether, apart from the question of optical activity, the isomerism of tropine and ψ-tropine might not be compared with that of borneol and *iso*borneol, depending on the orientation of the CH·OH group relatively to the loops of the ring system.

Dr. W. H. Mills pointed out that according to Willstätter's formula, although tropine contains two asymmetric carbon atoms, it is necessarily internally compensated and non-resolvable. For since three of the groups attached to the one asymmetric carbon atom are linked to the corresponding groups attached to the other, rearrangement of either of the asymmetric systems with respect to the other (so as to pass from, for example, a + + to a + − form) is impossible. The first asymmetric carbon atom is necessarily the mirror image of the second.

Since the planes of the piperidine and pyrrolidine rings are set at an angle, the relationship between tropine and ψ-tropine may be regarded as a case of *cis-trans*-isomerism, the hydroxyl in the CH·OH group being in the one case on the same side of the plane of the piperidine ring as the pyrrolidine ring, and in the other case on the other side.

Further, as the nitrogen atom is common to two rings lying in two different planes, it, together with its three valencies, will presumably lie in a third plane roughly bisecting the angle between the other two. The nitrogen atom will thus lie out of the plane of the rest of the piperidine ring, and consequently the *cis*- or *trans*-relationship of the hydroxyl group can also be referred to it.

***260. "Adsorption in relation to Gibbs's theory. The mercury adsorbing surface." By William Cudmore McCullagh Lewis.**

The author has continued his experiments carried out with a view to verify experimentally Gibbs's expression for adsorption. Determinations were made with aniline, caffeine, mercuric sulphate, and sodium glycocholate. The presence of electrocapillary and electrostatic effects was discussed, and a general application was made to the case of the mercury drop-electrode.

DISCUSSION.

Mr. A. E. DUNSTAN asked the author whether the gelatinisation of the colloidal dyestuffs mentioned by him occurred during the process of dyeing; if so, what was the specific function of the mordant?

Mr. LEWIS, in reply to Dr. Cain as to the rôle of adsorption processes in dyeing, suggested dyeing of fibres as due to simultaneous solubility effects in the bulk of the fibre with adsorption on the surface. That the process of dyeing cannot be simply adsorption is evidenced by the fact that a simple adsorption process in the sense of Gibbs' theory is a reversible one; that is to say, if the fibre colour were simply due to adsorption, repeated washing should remove it. The fastness is probably due to gelatinisation (an irreversible process) on the surface of the fibre.

261. "The electromotive behaviour of cuprous oxide and cupric hydroxide in alkaline electrolytes." By Arthur John Allmand.

Electrode systems containing copper, cupric hydroxide, and alkali are unstable, owing to the production of cuprous oxide. The following systems are stable: (*a*) Cu | Cu_2O alkali; (*b*) Pt $\left|\begin{matrix}Cu(HO)_2\\Cu_2O\end{matrix}\right.$ alkali. The single potential differences involved in these systems were measured. Sodium and potassium hydroxide were used in both *N*- and *N*/10-concentration. The auxiliary electrodes used were calomel (*N* and *N*/10), as hydrogen electrodes are found to behave unsatisfactorily in alkaline electrolytes. From the results of the measurements, the solubility products of cupric hydroxide and cuprous oxide were calculated. Theoretical values for the hydrogen electrode in alkaline solution were assumed, and the *E.M.F.* of the cell

$$Cu \mid Cu_2O \text{ alkali} \left|\begin{matrix}Pt\\H_2\end{matrix}\right.$$

thus obtained. From this was calculated the dissociation pressure of cuprous oxide at the ordinary temperature, and also the temperature

at which cuprous oxide will dissociate when heated in air. The figures show satisfactory agreement with those calculated from thermal data by the use of Nernst's theorem. The influence of the size of grain of depolariser on potential measurements was recognised and emphasised.

262. "The stereoisomeric modifications of $a\beta$-dibromobenzylacetophenone." By Ida Smedley.

The action of bromine on benzylideneacetophenone was originally investigated by Claisen (*Ber.*, 1887, **20**, 657), who added a molecular proportion of bromine to one of benzylideneacetophenone in chloroform solution; white needles melting at 157° separated, and were identified as the dibromo-additive product. Subsequently, the preparation of this substance was described by Wislicenus (*Annalen*, 1899, **308**, 219), and later by Ruhemann (*Trans.*, 1904, **85**, 456). The latter observer points out that a better yield of the dibromo-compound is obtained if the bromination is carried out in carbon disulphide solution.

On mixing together molecular proportions of bromine and benzylideneacetophenone in chloroform solution, crystals separated, which melted at 157—158° when recrystallised from alcohol, and were identical with the dibromo-derivative previously described; the yield of this was from 70 to 80 per cent. On further concentrating the solution, white needles melting at 111° crystallised out; recrystallisation from alcohol raised their melting point to 112—113°:

0·1718 gave 0·3033 CO_2 and 0·0512 H_2O. C = 48·15; H = 3·32.
0·2115 ,, 0·2158 AgBr. Br = 43·37.
0·2750 ,, 0·2796 AgBr. Br = 43·28.
$C_{15}H_{12}OBr_2$ requires C = 48·91; H = 3·26; Br = 43·47 per cent.

This compound is therefore isomeric with the benzylideneacetophenone dibromide melting at 157°.

The more soluble isomeride (m. p. 113°) becomes discoloured if the temperature is raised above its melting point, and shows signs of decomposition; after heating for some minutes at 180°, the dark-coloured residue which solidified on cooling was pressed on a porous plate and crystallised from alcohol; white needles were obtained, which melted at 156—157°. The identity of this substance with the less soluble isomeride was confirmed by the mixed melting-point method.

263. "The constituents of the fruit of Ecballium Elaterium." By Frederick Belding Power and Charles Watson Moore.

The results obtained by an examination of elaterium and of the "elaterin" therein contained (*Pharm. J.*, 1909, [iv], **29**, 501) have led the authors to undertake a complete investigation of the fruits of *Ecballium Elaterium*. One of the objects in view was to ascertain whether any evidence could be obtained in support of the statement by Berg (*Bull. Soc. chim.*, 1897, [iii], **17**, 85) that elaterin exists in these fruits in the form of a glucoside. The expressed juice of the fruit was found to contain, in accordance with a previous observation by Berg (*loc. cit.*), an enzyme which is capable of hydrolysing β-glucosides. For the purpose of a complete investigation, 27 kilograms of the fresh, nearly ripe fruit were employed. The alcoholic extract of this material yielded a quantity of resin, from which the following substances were isolated: a small amount of a hydrocarbon (m. p. 68°); a phytosterol, $C_{27}H_{46}O$ (m. p. 148°; $[\alpha]_D$ +3·2°); a substance (m. p. 258—260°) which appears to be related to ipuranol, $C_{28}H_{38}O_2(OH)_2$; a mixture of fatty acids; and a product corresponding to the so-called "elaterin," the characters of which have previously been elucidated by the authors (*loc. cit.*). It is now proposed to designate the lævorotatory constituent of crude elaterin as α-elaterin, and the dextrorotatory, physiologically active constituent as β-elaterin. The portion of the alcoholic extract which was soluble in water contained a quantity of inorganic salts and a sugar which yielded *d*-phenylglucosazone (m. p. 216°). It has been shown that the elaterin exists in *Ecballium* fruits in a free state, not in the form of a glucoside, and no evidence could be obtained of the presence of any glucosidic substance.

264. "3-Nitrodurene." By John Cannell Cain.

As all endeavours to prepare mononitrodurene by the direct nitration of durene have hitherto proved unsuccessful—the dinitro-derivative always being obtained—Willstätter and Kubli have recently (*Ber.*, 1909, **42**, 4151) prepared aminodurene by first converting durene into the monobromo-derivative, then nitrating this to bromonitrodurene which is finally reduced with zinc dust and acetic and hydriodic acids to aminodurene. These authors were able to prove that a small amount of nitrodurene is formed when iododurene is treated with silver nitrite, but as the nitrodurene is accompanied by much unchanged iodo-derivative, it could not be isolated in the pure state.

In continuation of his investigation of the derivatives of durene (*Ber.*, 1895, **28**, 967), the present author, in the year 1895, prepared

nitro- and amino-durene, but as the work was interrupted the results were not published.

3-Nitrodurene, $C_6HMe_4 \cdot NO_2$, is readily obtained in good yield by diazotising 3-nitro-6-aminodurene (*loc. cit.*) in alcoholic solution and boiling until no more nitrogen is evolved. The solution is poured into water and distilled in a current of steam, when the pure nitro-hydrocarbon passes over as an oil which, on cooling, solidifies to colourless crystals melting at 70°. On boiling nitrodurene with tin and hydrochloric acid it is reduced to the amino-compound, which was, however, not further characterised.

265. "Chemical affinity and electrons." (Preliminary note.) By Bernhard Flürscheim.

In a recent paper it has been pointed out that the relations between molecular constitution and dissociation constants do not support the idea that atoms are linked by means of interposed electrons; since numerous organic reactions lead to the same conclusion, the author put forward the following alternative hypothesis:

(1) The atomic mass (or aggregate of positively and negatively charged particles) is surrounded by an ethereal layer or envelope, in which, by the action of free electrons within the atom, the form of energy called chemical affinity is induced similarly to the induction of molecular magnetism through Ampère currents.

(2) The affinity thus induced varies, for different atoms, both in quantity and in quality. Its quantity depends on the capacity of the ethereal envelope, which is proportional to the surface of the uncombined and uncompressed atom. Its quality is a function of the electrical charges within the atom. If the latter contains equal amounts of positive and negative charges, no affinity is induced (inert gases: compare A. Michael, *J. pr. Chem.*, 1903, [ii], **68**, 487). If positive or negative charges are in excess, the induced affinity assumes corresponding polarity. Its specific polarity, that is, the atom's polar affinity (A_p) per unit of its total affinity (A), corresponds with the proportion of the number (n) of excess of electrical charges (e) to the surface of the uncombined atom (s_u): $Ap/A = k \times ne/s_u$. The relative polarity of the atom is its specific polarity, expressed in fractions of maximal, that is electronic, polarity: $A_{pr} = A_p/A \times e$.

(3) When two atoms are combined, their ethereal envelopes are contracted toward the point of linking, as a result of their mutual attraction. Thereby the atomic mass is compressed, until its resistance to compression produces an equilibrium (compare I. Traube, *Ber.*, 1907, **40**, 729). This resistance is a function of the density of the

uncombined atom, $F(d)$, and of its specific polarity, $F_1(A_p/A)$. Between the force of mutual attraction (Q) of two atoms, their uncombined volumes (v_u), and their volumes in combination (v), we accordingly have the relation:

$$v = \frac{k_1 \times v_u \times F(d) \times F_1(A_p/A)}{Q}.$$

Q is the algebraic sum of the forces emanating from the polar (A_p) and non-polar (A_{np}) components of the affinities of the two atoms I and II, and r being the distance of the atomic centres:

$$Q = \frac{k_2 \times A_{np_I} \times A_{np_{II}} \pm k_3 \times A_{p_I} \times A_F{}^{II}}{r^2}$$

$\pm$ becomes + for heteropolar and − for isopolar atoms, in which latter case atomic combination may become labile (fluorine) or cease (many metals).

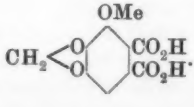
When one atom is linked to several others, Q and v for all are the results of an equilibrium (compare *J. pr. Chem.*, 1907, [ii], **76**, 185).

(4) Atoms transfer their own polarity to other atoms in proportion to the force with which they are linked to them.

(5) These views are supported by ample evidence, especially by the changeable valency of strongly polar atoms, by substitution reactions, molecular volumes, and thermochemical constants. They are capable of throwing new light on various problems. Regarding migration velocity in electrolytes, for instance, it is seen that all existing calculations of ionic hydration based on conductivity measurements require modification; for they all assume that the electrodes attract the constant ionic charges, e, whereas only that part of e which is not bound by the atomic affinity of the solvent and solute can exert any attraction on the electrodes; and this free portion of the electronic charge varies from ion to ion, being the outcome of an equilibrium, as explained above.

266. "Synthesis of cotarnic acid." By William Henry Perkin, jun., Robert Robinson, and Frederick Thomas.

Starting with 5 : 6-methylenedioxy-1-hydrindone, the authors have succeeded in synthesising cotarnic acid in a way which clearly proves that its constitution is that represented by the usually accepted formula:



267. "The acyl-bornylamines. Part I. Fatty bornylamides." By Percy Faraday Frankland and Fred Barrow.

These compounds have been studied in connexion with the relationship between chemical constitution and optical activity. The authors have prepared the formyl, acetyl, *propionyl*, and n-*butyryl* derivatives, and have determined their rotatory power in methyl and ethyl alcohol, in glacial acetic acid, and in pyridine solution respectively. The formyl and acetyl compounds have been previously prepared and optically examined in ethyl-alcoholic solution by Forster (Trans., 1899, **75**, 934, 1149).

268. "The acyl-bornylamines. Part II. Aromatic bornylamides." By Percy Faraday Frankland and Fred Barrow.

In continuation of the above work (preceding abstract), the authors have prepared the benzoyl, the o-, m- and p-*toluyl*, and the o-, m- and p-*nitrobenzoyl* derivatives. The optical activity was determined in methyl and ethyl alcohol, in glacial acetic acid, and in pyridine solution respectively. The benzoyl compound had been previously prepared by Forster (*Trans.*, 1898, **73**, 393), and its optical activity determined in ethyl-alcoholic solution.

For purposes of comparison, some hitherto unpublished results obtained by one of the authors and Miss M. B. Thomas with the *tartaronitroanilides* (o-, m-, and p-) were described.

269. "Synthesis of *cyclo*hexanone-3-carboxylic acid." By Mary Elizabeth Dobson, John Ferns, and William Henry Perkin, jun.

The authors have prepared *ethyl pentane-aδδε-tetracarboxylate*, $CO_2Et{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, and find that this ester reacts with sodium with the formation of *ethyl* cyclo*hexanone*-3 : 6-*dicarboxylate* (I):

$$CO_2Et{\cdot}CH\langle\begin{matrix}CO-CH_2\\CH_2{\cdot}CH_2\end{matrix}\rangle CH{\cdot}CO_2Et \qquad (I.)$$

$$CH_2\langle\begin{matrix}CO-CH_2\\CH_2{\cdot}CH_2\end{matrix}\rangle CH{\cdot}CO_2H. \qquad (II.)$$

On hydrolysis and elimination of carbon dioxide, this ester yields *cyclo*hexanone-3-carboxylic acid (m. p. 73—75°) (II), which had previously been prepared by Perkin and Tattersall (*Trans.*, 1907, **91**, 480) from *m*-hydroxybenzoic acid by reduction and oxidation of the *cyclo*hexanol-3-carboxylic acid so produced with chromic acid mixture.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Abegg, *Richard,* and **Sackur,** *O.* Physikalisch-Chemische Rechenaufgaben. pp. 104. Leipzig 1909. (*Recd.* 21/10/09.)
From the Publisher: G. J. Göschen.

Hollard, *A.,* and **Bertiaux,** *L.* Analyse des métaux par électrolyse. 2nd edition. pp. 256. Paris 1909. (*Recd.* 21/10/09.)
From the Publishers: Messrs. H. Dunod et Pinat.

Mees, *Charles Edward Kenneth.* An atlas of absorption spectra. pp. 74. ill. London 1909. (*Recd.* 30/9/09.) From the Author.

Meyer, *Kirstine.* Temperaturbegrebets Udvikling gennem Tiderne samt dets sammenhæng med vexlende Forestillinger om Varmens Natur. pp. 182. Copenhagen 1909. (*Recd.* 8/9/09.)
From the Author.

Musu-Boy, *Roberto.* Lo Zinco. pp. xvi + 219. ill. Milano 1909. (*Recd.* 21/10/09.) From the Publisher: Ulrico Hoepli.

Richards, *Theodore William,* [and others]. Experimentelle Untersuchungen über Atomgewichte. pp. viii + 890. ill. Hamburg 1909. (*Recd.* 21/10/09.) From the Publisher: Leopold Voss.

Savoia, *Umberto.* Metallografia. pp. xvi + 208. ill. Milano 1909. (*Recd.* 21/10/09.) From the Publisher: Ulrico Hoepli.

II. *By Purchase.*

Handbuch der anorganischen Chemie. Edited by *Richard* **Abegg** and *Fr.* **Auerbach.** Vol. III. Part II. pp. xii + 921. Leipzig 1909. (*Reference.*)

Birckenbach, *L.* Die Untersuchungsmethoden des Wasserstoffperoxyds. (Die chemische Analyse, Vol. VII.) Stuttgart 1909.

PRESENTATION TO PROFESSOR KOERNER.

A Committee has been formed in Milan with the object of celebrating the seventieth birthday of Professor Koerner. It is proposed to devote subscriptions to the following purposes:

1. Foundation of a prize for work in pure and applied chemistry.
2. Reprinting Professor Koerner's works.
3. Presentation of a gold medal to Professor Koerner.

The Treasurer of the Chemical Society will be glad to receive subscriptions, and will forward them to the Organising Committee.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, 6th December, 1909.

All persons who received grants in December, 1908, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Wednesday, 1st December.

The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal tar and allied industries.

At the next Ordinary Scientific Meeting on **Thursday**, December **2nd**, 1909, at **8.30** p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated:

"A new method for the detection of sodium, calcium, and rubidium." By W. C. Ball.

"The correction of the specific gravity of liquids for the buoyancy of air." By J. Wade and R. W. Merriman.

"Synthesis with the aid of monochloromethyl ether. Part II. The action of monochloromethyl ether on the sodium derivative of ethyl acetoacetate." By J. L. Simonsen and R. Storey.

"Synthesis of hordenine, the alkaloid from barley." By G. Barger.

"Note on Dr. Scott's paper on the molecular weight of tetra-ethylammonium bromide and the atomic weight of carbon." By Sir Edward Thorpe.

"The relation between the chemical constitution of monoazo-dyes and their fastness to light." By E. R. Watson, A. C. Sirkar, and J. M. Dutta.

"Synthesis in the epinephrine series." By F. Tutin, F. W. Caton, and A. C. O. Hann.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, December 2nd, 1909.

Aiyer, A. K. Yegna Narayan,
Bangalore, India.

Assistant Chemist, Department of Agriculture, Mysore State. Master of Arts and Gold Medallist in Chemistry of the University of Madras (India) and eight years' experience as Assistant Chemist in the Department of Agriculture, Mysore.

Morris W. Travers. H. V. Krishnayya.
M. Goolab Roy. *Claude S. Fawcitt.*

Anklesaria, Jehangir Dhanjishaw,
Ahmedabad, India.

Pharmaceutical Chemist. Minor and Major Qualifications of the Pharmaceutical Society.

Arthur W. Crossley. Chas. Horne Warner.
Charles Gilling. *W. Palmer Wynne.*
M. O. Forster.

Armstrong, James Alexander Hadden,
Dumisa, Natal.

Solicitor, Notary Public, Geologist and Metallurgist, presently acting as Metallurgist to the Dumisa Gold Mining Co. The holder of several certificates from Oxford and Cape Universities. Conducted much scientific research. Vide Annals S.A. Association for Advancement of Science (1907). Read a paper before the S.A.

Association on "Diamondiferous and Sedimentary Deposits of Natal."

S. R. Edminson. Carl Lewis.
A. M. Neilson. *E. H. Croghan.*
W. J. Wren.

Barker, Donald William Elsom,
2, Hope Street, Wrexham, N. Wales.

Manufacturing Chemist and Optician. Past Student of Muter's School of Pharmacy. Member of the Pharmaceutical Society of Great Britain. Member of the Society of Chemist Opticians. Have been engaged in Manufacturing and Analytical Chemistry for over twelve years. My desire is to be up to date in the various branches of research work.

John Muter. William D. Rogers.
John T. Fleet. A. H. M. Muter.
Will. F. Mawer.

Baron, Harold, B.Sc.,
21, Underhill Road, East Dulwich, London, S.E.

Chemist, Westinghouse Patent Bureau, 2, Norfolk Street, Strand, W.C. Graduated Bachelor of Science, First Class Honours in Chemistry, Victoria University, 1903; Joint Author of "Formation and Reactions of Imino-compounds, Part I" (*J.C.S.*, 1904); Author of Gartside Report, No. 8, "Chemical Industry on the Continent."

Harold B. Dixon. W. H. Perkin.
Arthur Lapworth. Norman Smith.
H. F. Coward.

Best, Stanley Robert, M.Sc.,
Hope Villa, Wellington Road, Whalley Range, Manchester.

Master of Science, Analyst and Assistant-Manager. Research Assistant to Dr. Jocelyn F. Thorpe, F.R.S., 1908–09, and have published four papers conjointly with him in the Journal of the Society, namely, *Trans.*. 1909, **95**, 8; *ibid.*, 261; *ibid.*, 685; *ibid.*, 1508.

Harold B. Dixon. J. L. Simonsen.
W. H. Perkin. A. N. Meldrum.
J. F. Thorpe. R. Robinson.

Bottomley, Hubert Frederick,
The Cedars, Wavertree Road, South Woodford, Essex.

Chemist. At present and for the past three years engaged as assistant in Chemical and Bacteriological research in connexion with

Sanitary Chemistry for the Sanitas Co., Ltd., London. Previous to the above I assisted in experiments on the Chemical and Bacterial treatment of Sewage at Huddersfield.

C. T. Kingzett, W. E. Speight.
R. C. Woodcock. James Bruce.
R. M. Harland.

Breakspear, Henry Shaw,
20, Walton Well Road, Oxford.
Science Master. B.A. (Oxon.), Honours in Chemistry.
W. W. Fisher. N. V. Sidgwick.
Allan F. Walden. T. S. Moore.
F. D. Chattaway.

Burger, Dr. O. K. H.,
4, Mission Row, Calcutta.
Analytical and Consulting Chemist. Ph.D. (Munich). Assistant at the Chemical Laboratory of the State in Munich (January, 1906–October, 1907). Publications: Author of several communications on Inorganic Chemistry, published in the *Berichte der deutschen Chemischen Gesellschaft*. Wishes to keep in touch with current literature while in India.

E. Sommerfeldt. Adolf von Baeyer.
Paul Brühl. William Tate.
R. Willstätter. *W. H. Perkin.*

Bury, Frank Ward,
Lyndale Cottage, Darwen, Lancs.
Science Teacher, Hebden Bridge Secondary School, Yorks. B.Sc. Manchester. Teacher in Chemistry. Desire to keep abreast of researches in Chemistry.

Harold B. Dixon. H. F. Coward.
W. H. Perkin. R. Robinson.
Norman Smith. *Arthur Lapworth.*

Callister, William Edward, B.Sc. (Manc.), L.C.P.,
The Rowans, Onchan, Isle of Man.
Science Master, Douglas Secondary School. Assistant Science Master and Teacher of Chemistry at St. Margaret's Secondary School, Manchester, 1902–1904. Senior Science Master and Teacher of Chemistry at the Douglas Secondary School, Isle of Man, 1904 to present time.

Fred. R. Grundey. *Frank Dixon.*
R. L. Taylor. *J. L. Simonsen.*
H. F. Coward. *W. H. Perkin.*

Carey, William Gordon,

"Wyngarth," Harpenden, Herts.

Analytical Chemist. Certificated Day Student in Chemical Department at City and Guilds Technical College, Finsbury (1901–1904). Analytical Chemist to the Clinical Research Association (1904–1909). Associate of Institute of Chemistry (Branch E).

R. Bodmer. J. S. H. Walker.
Charles A. Keane. *A. Prideaux Davson.*

Edward Hinks.

Chamblis, Hardee,

56 W. 36th St., New York City, U.S.A.

Chemist for past six years on the Research Staff of the General Chemical Company, New York. M. S. Vanderbilt University (1899), where I was Scholastic Fellow. Ph.D. Johns Hopkins University (1900). Dissertation, "The Permanganates of Mg, Zn, and Ca." Assistant in Chemistry, Columbia University, New York City (1900–01). Chemist, Moore Electrical Company, Newark, N.J., Patentees of More Tube Lights.

T. Lynton Briggs. Friend E. Clark.
Wm. L. Dudley. Chas. Baskerville.

H. T. Vulté.

Chand, Lakshami,

c/o Messrs. Ramchand, Bulaki das Naudau Sahni Street, Benares City, U.P. India.

Student of the Municipal School of Technology, Victoria University. Manchester. B.A. of Allahabad University in English literature, B.Sc. (Tech.) of Victora University, Manchester. Desirous of keeping in touch with modern chemical research.

E. L. Rhead. S. J. Peachey.
F. G. Richards. Jas. Grant.

C. Stanley Gibson.

Dawson, James Ferguson,

Glencoe House, Tarbert, Loch Fyne, N.B.

Science Master. Bachelor of Science of the Manchester University. Science Master in the Higher Grade School, Tarbert, Loch Fyne, Scotland. Late Junior Science Master in the Academy, Alloa.

Harold B. Dixon. W. H. Perkin.
H. F. Coward. J. F. Thorpe.

R. Robinson.

Dunningham, Alfred Charles,

28, Victoria Road, Northwich, Cheshire.

Schoolmaster (Science). Student at University College, London

(October, 1904—March, 1908). Internal Graduate in Science, of London University, with 2nd Class honours in Chemistry. At present Science Master in Sir John Deane's Grammar School, Northwich.

R. W. Gray. Samuel Smiles.
N. T. M. Wilsmore. E. de Barry Barnett.
Edward C. Cyril Baly.

Edgar, Edward Charles, D.Sc.,
Dalegarth, Romiley, Cheshire.

Lecturer in Chemistry in the Manchester University. Joint author, with Prof. Dixon, of memoir on "The Atomic Weight of Chlorine," *Phil. Trans.* R.S., 1905, and author of second memoir on "The Atomic Weight of Chlorine," *Phil. Trans.*, 1908.

Harold B. Dixon. Norman Smith.
W. H. Perkin. H. F. Coward.
Arthur Lapworth. W. N. Haworth.
R. Robinson.

Edge, Alfred,
Ravenhurst, Clayton Bridge, Manchester.

Technical Chemist to the Berlin Aniline Co., Limited. Student for the full course at the Municipal Technical School, Manchester, and for two years at the Owens College, Manchester. Demonstrator in the Chemical Dept. Manchester Technical School. Works chemist at Messrs. J. Mandleberg & Sons, Rubber Manufacturers, Pendleton, Manchester, and as above.

E. L. Rhead. Jas. Grant.
F. G. Richards. Jul. Hübner.
F. S. Sinnatt. *C. Stanley Gibson.*
S. J. Peachey.

Edwards, Frederick Watson,
64, Coppice Side, Swadlincote.

Photographer and Journalist. Contributions to Photo-chemical Science in *The Amateur Photographer* and *The Practical Photographer*: "Prussian Blue and Turnbull's Blue: Their Application in Photography"; "The Theory and Practice of Gold Toning"; "Pigments and Dyes: Their Application in Photography"; "A Ferrocyanotype Process"; "Factorial Development with Ferrous Oxalate"; "The Ferrous Oxalate Developer"; "On Tinting Negatives"; "Hardening Negatives." Lectured on Radium, Polonium, and Photo-chemical

subjects before Burton Natural History Society and the local Photographic Societies.

Arthur Slator. Jas. O'Sullivan.
S. L. Courtauld. *Chas. Geo. Matthews.*

A. L. Stern.

Ewins, Arthur James,

7, Towton Road, West Norwood, S.E.

Research Chemist. B.Sc. (Lond.); joint author (with G. Barger) of various papers in the *Trans. Chem. Soc.* during the last four years.

George Barger. J. Bernard Coleman.
George Stanley Walpole. J. C. Crocker.
F. H. Lowe.

Forrester, George Peters,

69, Beck Strasse, Darmstadt (Germany).

Member of the Scientific Staff of E. Merck. Studied at University of Heidelberg, 1904–1906, under Professors Curtius, Bredig, Quincke, Pfitzer, Jannasch, Stollé, Glück, Neumann. Passed German Pharmaceutical State Examination with Note I. Collaborated with Mr. Peter MacEwan in communication to the International Congress of Applied Chemistry on "Variations in the Activity of Certain Toxic Drugs." Elected Continental Secretary of the Commission to give effect to the Congress resolution on the subject.

Peter MacEwan. *N. H. Martin.*
C. R. Hennings. *E. F. Harrison.*
Leonard Dobbin. *F. B. Power.*

Forshaw, Arthur,

104, Holly Road, Handsworth, Birmingham.

Research Chemist, John Wright and Eagle Range Co., Essex Works, Birmingham. M.Sc., Honours in Chemistry (Manchester). Late Fellow of Leeds University. Author of memoir on "Efficiency of Different Gases for Illuminating Power," *Trans. Inst. Gas Engineers.*

Harold B. Dixon. J. F. Thorpe.
W. H. Perkin. J. L. Simonsen.
Norman Smith. R. Robinson.

Arthur Lapworth.

Freymuth, William Adolf,

Rangoon, Burma, India.

Analytical and Consulting Chemist in Rangoon, Burma, India. Preliminary chemical training under C. M. Stuart, Esq.; two years

Charlottenburg not completed, lack of money; some research under Stuart; Metallurgy under H. L. Sulman, Esq.; eight years' service with Sulman and Picard; special jobs, Cyanide Chemistry, Hungary, Venezuela, Italy. Sent to Moreing, Frecheville, Curle, etc., as Metallurgical Assistant on mine examinations. Metallurgical Process Research under Sulman and Picard. Management of Exploration Company, Burma, five years. Assoc. Member Institute of Mining and Metallurgy. Last two years spent on research in manufacture of lac. Discovery of greatly improved process of manufacture of refined lac. This and other manufacturing processes now under management in Rangoon and Calcutta.

Charles M. Stuart. Thos. R. Duggan.
Frank L. Teed. *H. Mansfield.*
M. Kemp-Welch.

Fürstenhagen, Otto,
28, Schlesische Strasse, Berlin, S.O.

Technical Chemist to the Actien-Gesellschaft für Anilin Fabrikation, Berlin. Publications: "The Theory of Dyeing," "A New Group of Wool Dyes," "Some New Colouring Matters," "Some New Cotton Dyes," etc.

Jul. Hübner. *E. L. Rhead.*
J. R. Appleyard. *S. J. Peachey.*
C. Rawson. *F. G. Richards.*
Walter M. Gardner. *F. S. Sinnatt.*
C. Stanley Gibson. *Jas. Grant.*

Furneaux, George Pomeroy,
"Harbour View," Brixham, S. Devon.

Science Master at Tettenhall College, Staffordshire. B.A. (Oxon.), Second Class Honours (Chemistry).

W. W. Fisher. H. Brereton Baker.
Allan F. Walden. Andrea Angel.
N. V. Sidgwick.

Gardiner, Alexander David,
6, Wellfield Terrace, Springburn, Glasgow.

Analytical Chemist. Studied Chemistry, Metallurgy, and Bacteriology at the Glasgow and West of Scotland Technical College. For the last nine years Assistant to F. W. Harris, Esq., F.I.C., Public Analyst for Glasgow.

F. W. Harris. T. Cockburn.
Thomas Gray. Andrew S. Matchet.
A. Humboldt Sexton.

Gardner, Henry Dent, jun., M.Sc.,
Fairmead, The Goffs, Eastbourne.

Research Chemist. Passed B.Sc. and M.Sc. Examinations in Chemistry of University of Manchester. Joint author of "Researches on Anthraquinones and Phthaleins," in *Journal Chemical Society*, 1907.

Harold B. Dixon.	H. F. Coward.
W. H. Perkin.	J. L. Simonsen.
A. N. Meldrum.	R. Robinson.

Harding, Victor John, M.Sc.,
Lonsdale Terrace, Whitefield, Manchester.

Research Chemist. B.Sc. Manchester. 1st Class Honours in Chemistry, 1906. M.Sc. 1907. University Scholar and Beyer Fellow. Joint author of "Experiments on the Synthesis of Hexylidene-acetic Acid, Part II," and of other papers in *Journal of Chemical Society.*

Harold B. Dixon.	R. Robinson.
W. H. Perkin.	H. F. Coward.
Norman Smith.	W. N. Haworth.

Arthur Lapworth.

Harvey, Arthur John,
88A, East India Dock Road, Poplar.

Assistant Chemist to Messrs. E. Cook & Co., Ltd., Bow (Soap-makers), and Lecturer on "Soap Manufacture" at East Ham Technical College. First Class Certificate and Bronze Medal "Soap Manufacture" City and Guilds, London. First Class Certificates, Stage III, Board of Education, both Inorganic and Organic Chemistry. Member of the Society of Chemical Industry.

A. E. Dunstan.	F. Henry Streatfeild.
W. H. Barker.	George Dean.
R. W. Wilson.	S. Godfrey Hall.

Hendry, Robert Douglas,
3, Glebe Terrace, Alloa.

Chemist and Manager of Dyeworks. Trained as Chemist at Nottingham University College; Chemist and Manager for twelve years to Messrs. John Paton, Son & Co., Ltd., Alloa. Has specially studied Chemistry in its relation to wool and colour, and lectured on these and allied subjects. Wishes to become a Fellow for the purpose of keeping in touch with the latest thought and methods in the chemical world.

Wm. B. Jackson.	F. W. Harris.
Alec B. Steven.	*Thomas Gray.*

William S. Denham.

Holmyard, Eric John,

7, Manor Street, Cambridge (Sidney Sussex Coll.).

University Undergraduate in Science. Keenly interested in Chemical Research and Chemistry generally. Intend to specialise in Chemistry.

F. W. Dootson.	C. Stanley Gibson.
A. E. Bellars.	J. G. M. Dunlop.
H. O. Jones.	H. J. H. Fenton.

Leech, Benjamin,

Beech Knoll, Macclesfield.

Dyer and Chemist. M.A. Cantab. (Nat. Sci. Trip., Pt. I, 1899; Pt. II, 1900). Formerly Scholar of Clare Coll., Cambridge.

Horatio Ballantyne.	H. J. H. Fenton.
S. Ruhemann.	H. O. Jones.

William H. Ballantyne.

Lewis, William Cudmore McCullagh,

Garmoyle, Bangor, Ireland. London Address: Chem. Lab., University College, Gower Street, W.C.

Student. Degree: M.A. (R.U.I.). Queen's College, Belfast; Liverpool University; Heidelberg University; University College, London. Publications: "Adsorption in Relation to Gibbs Theory," *Phil. Mag.*, April (1908); "On Sodium Glycocholate," *Biochem. Journal*, Vol. III, No. 3 (1908); "Adsorption" (second paper), *Phil. Mag.*, April (1909); "Zur elektrischen Ladung der Silberkolloide," *Zeitsch. für Kolloide*, Bd. IV., Heft 5; "Oel Wasser Emulsionen," *Zeitsch. für Kolloide*, Bd. IV., Heft 5, 1909.

William Ramsay.	F. G. Donnan.
Edmund Albert Letts.	A. J. Allmand.
J. Norman Collie.	N. T. M. Wilsmore.

Lundholm, Carl Olof, F.I.C.,

2, Eton Avenue, Hampstead, N.W.

Consulting Chemist to the Nobel Dynamite Trust. Diploma as Chemical Engineer from the Technical High School, Stockholm, 1870. Publication in *Teknisk Tidskrift*, Stockholm: "Manufacture of Fulminate of Mercury." Chemist to Nobel's Explosives Co., Ltd., from October, 1878 to May, 1889. Works Manager, Nobel's Explosives Co., Ardeer Factory, from 1/6/89 to 30/6/09.

T. E. Thorpe.	Otto Hehner.
Henry de Mosenthal.	Oscar Guttmann.
Alfred Gordon Salamon	*Arthur R. Ling.*

B. E. R. Newlands.

Norris, Roland Victor,

1, Howe Street, Higher Broughton, Manchester.

Schunck Research Assistant in Chemistry, Manchester University. B.Sc. (Honours) 1908, M.Sc. 1909. Joint author of papers on the "Derivatives of Naphthacene-quinone" and of "Anthraquinone," in the *Journal of Chemical Society.*

Harold B. Dixon. Norman Smith.
W. H. Perkin. H. F. Coward.
R. Robinson.

Ping, Francis Hugh,

10, Forest Place, Whipps Cross Road, Leytonstone, N.E.

Teacher. Associate of the Royal College of Science (in Chemistry), 1904–07. Science Master in Jamaica College, Kingston, Jamaica, 1908–1909 (May).

M. O. Forster. Chapman Jones.
James C. Philip. G. T. Morgan.
William A. Tilden.

Proud, Charles,

12, Chancellor Road, Southend-on-Sea.

Teacher of Chemistry. Teacher of Chemistry at Technical School, Southend, seven years. Science Student at Univ. Coll., Nottingham, three years. Student of Chemistry at the East London College since Jan., 1909.

F. Stanley Kipping. J. T. Hewitt.
Clarence Smith. F. G. Pope.
J. J. Fox.

Ritchings, Walter,

89, Rosehill Road, Burnley.

Science Master, Burnley Gram. Sch. Lecturer in Inorganic and Organic Chem., Burnley Tech. Institute. Degree of M.Sc. Manch., with First Class Honours in Chemistry. Woodiwiss Exhibitioner in Inorg. Chem., Owens College, 1902. Science Master at Burnley Gram. Sch. for five years. Lecturer in Hons. Chemistry, Burnley Tech. Sch., three years.

Harold B. Dixon. R. Robinson.
W. H. Perkin. W. N. Haworth.
J. F. Thorpe. *A. N. Meldrum.*
H. F. Coward. *F. Thomas.*

Robinson, Frederic William,

Grove House, Farnworth, Widnes.

Research Student. B.Sc., First Class Honours, Chemistry (Liverpool). Research on Double and Triple Ferrocyanides.

J. Campbell Brown. W. Collingwood Williams.
Henry Bassett, jun. A. W. Titherley.
F. G. Donnan.

Sabherwal, Pindi Das,

Bhera (Panjab), India.

Student, University College, Reading. Cambridge University Diploma in Agriculture. Oxford and Reading Joint Committee (Diploma in Agriculture). Passed General Chemistry in Part I, and Agricultural Chemistry in Part II, of National Diploma in Agriculture.

J. K. H. Inglis. John W. Taylor.
E. K. Hanson. J. W. Dodgson.
W. W. Fisher.

Sinha, Manindra,

Calcutta, India.

Senior Demonstrator in Chemistry, St. Xavier's College, Calcutta, India. A graduate (with special mention in Chemistry), Senior Demonstrator in Chemistry, St. Xavier's College. Member Calcutta Chemical Club (under the Presidentship of Dr. P. C. Rây).

P. C. Rây. Haradhan Ray.
Atul Chandra Ganguli. Punchānan Neogi.
Bidhu Bhushan Dutt.

Stanford, Spencer Boyd Oortis-,

Glenwood, Dalmuir, Dumbartonshire.

Chemical Manufacturer (Works address: 123, Mansion Street, Possilpark, Glasgow). Studied Chemistry at the Glasgow and West of Scotland Technical College; afterwards Assistant Analyst in the Glasgow Corporation Chemical Laboratory. For five years I was Chief Chemist and Assistant Manager of the Glasgow Corporation Sewage Department. At present senior partner of the firm of Stanford and Wylie, Chemical Manufacturers, Glasgow. Desirous of becoming a member of the Chemical Society to keep myself in touch with the progress of Manufacturing and Scientific Chemistry.

Wm. B. Jackson. Thomas Tyrer.
F. W. Harris. *D. Lloyd Howard.*
T. Cockburn. *John C. Umney.*
Chas. Umney.

Stephenson, Guy,

Alexandra Terrace, Crook, County of Durham.

Analytical Chemist. Studied Analytical Chemistry for four years under Messrs. Pattinson and Stead, Middlesbro'. Had charge of laboratory for six years, at Crook. Chief Chemist to Messrs. Pease and Partners, Ltd., Crook, for six years. Nature of work: Analysis of the following—Coke, Coal, Ironstone, Limestone, Fire Clay, Bricks, etc.; all the Tar Products made on the Plant. Water Analysis; and Chemical supervision of the working of the various plants.

J. C. Stead. Ernest W. Jackson.
H. Frankland. Alfred Hutchinson.

William A. Bone.

Stones, George Bertram,

Bank Villas, Tyldesley, near Manchester.

Teacher of Chemistry. M.Sc. (Victoria University, Manchester). One year Private Assistant to Prof. W. H. Perkin, Victoria University, Manchester. Teacher of Chemistry at Bablake Secondary School, Coventry, since September, 1906.

W. H. Perkin. R. Robinson.
J. L. Simonsen. W. N. Haworth.
J. F. Thorpe. H. F. Coward.

Strachan, James Thallon,

10, Nelson Street, Sunderland.

Technical Chemist. Student at Heriot-Watt College (Evening Chemistry Classes), Edinburgh (1898–1902); Assistant Chemist in laboratory of J. and G. Cox, Ltd., Glue and Gelatine Manufacturers, Gorgie Mills, Edinburgh (Sept., 1901, to Oct., 1903); Day Student at Heriot-Watt College, Edinburgh (Oct., 1903, to Nov., 1906); Courses in Chemistry: Inorganic, Organic, Physical and Technical (Theor. and Pract.); Advanced Sound, Light and Heat, and Electricity and Magnetism (Theor. and Pract.); Advanced Mathematics (Pure and Applied); Short Course in Microscopical and Bacteriological work (Edinburgh University Higher Prelim.). Demonstrator in Chemistry to First Year Evening Class Students, Heriot-Watt College (Oct., 1903, to Nov., 1905). Demonstrator in Chemistry to First Year Day Class Students, Heriot-Watt College (Nov., 1905, to Nov., 1906). Chemist, Hendon Paper Works Co., Ltd., Sunderland (since Nov. 1906). Elected Member of Society of Chemical Industry (April, 1909). Desirous of keeping in touch with all the recent developments in Chemical Science.

J. Gibson. C. F. Baker.
J. P. Longstaff. Chas. Meads.
A. P. Laurie. *Leonard Dobbin.*

Taplin, Edward Walter,

Church House, Heavitree, Exeter.

Brewer and Brewer's Chemist. For the past eleven years have been engaged as a Brewer and Brewer's Chemist and Analyst. Hold the Silver Medal in Honours (Full Technological Certificate) of the City and Guilds of London Institute's Examination in Brewing. Two pupils of mine have also taken the Silver Medal in Honours. Am interested in Manufacturing Chemistry generally, especially as applied to brewing and the carbohydrates, and desire to keep in touch with current developments in Chemistry.

F. W. Brown.	*Arthur Smithells.*
Alfred C. Young.	*Thomas Fairley.*
Alf. Chaston Chapman.	*H. W. Watson.*
A. J. Murphy.	*B. A. Burrell.*

Thoms, Professor Dr. Hermann,

Berlin-Steglitz, Hohenzollernstr. 3.

Universitätsprofessor. Direktor des Königlichen Pharmazeutischen Instituts der Universität Berlin, als solcher verpflichtet Vorlesungen über Pharmazeutische Chemie, Toxikologische Chemie ü. Nahrungsmittelchemie zu halten.

Frederick B. Power.	Peter MacEwan.
Frank Tutin.	W. L. Howie.

E. F. Harrison.

Tingle, Joseph Grantley,

Nauru, Marshall Islands, Central Pacific.

Chemist on Nauru to the Pacific Phosphate Co., Ltd., Leadenhall Street, London; Melbourne and Sydney. Many years engaged in analytical and other chemical work in London, India, Australia, and the phosphate islands of the Pacific.

E. F. Harrison.	W. Phillip Want.
Peter MacEwan.	C. Edwd. Sage.
E. J. Millard.	*John C. Hewlett.*

Tizard, Henry Thomas,

23, Geneva Road, Kingston-on-Thames.

B.A. Oxford, 1908. Engaged in Research in Chemistry.

D. H. Nagel.	J. E. Marsh.
N. Garrod Thomas.	F. D. Chattaway.
Harold Hartley.	N. V. Sidgwick.
Allan F. Walden.	T. S. Moore.

D. L. Chapman.

Turner, Herbert,

217, Middleton Street, Moss Side, Manchester.

Form Master; Certificated Teacher, St. Margaret's Higher Elementary School, Manchester. Bachelor of Science (Physics and Chemistry) Univ. of Manchester. In addition to usual three years' training, also two years' special work in Chemistry and Physics at the Manchester University and School of Technology. Two years' work in the University of Leeds in classes specially conducted for the training of Science-teachers.

R. L. Taylor. Harold B. Dixon.
G. H. Bailey. *W. H. Perkin.*
J. L. Simonsen.

Van Essen, Everard Cecil,

28, Hereford Road, Snaresbrook, N.E.

Analytical and Technical Chemist. Chemist since 1905 to Messrs. Hemingway and Co., Colour and Chemical Manufacturers, Marshgate Lane, Stratford, London, E. Formerly (1902–1905) Chief Assistant to Arthur P. Strohmenger, Esq., Analytical Chemist and Electrometallurgist, Caxton House, Westminster, S.W.

A. M. Glass. Arthur P. Strohmenger.
Frank Hemingway. *B. E. R. Newlands.*
Stanley J. Peachey. *Watson Smith.*
Bernard Dyer.

Waliaschko, Nikolai,

Hohenzollernstr. 12, II, l., Leipzig, Deutschland.

Magister der Pharmacie und Magistrant der Chemie der Universität, Charkoff (Russland). Als Privatdozent der Chemie und Pharmacie hat der Unterzeichnete die Vorlesungen über die Pharmazeutische Chemie, über die Organische Chemie und über die Stereochemie in Jahren 1906–8 in der Universität Charkoff gehalten. *Gedrückte Arbeiten*: "Ueber das Adonidin Pharmaz. Bote" (russisch), 1902; "Ueber die Konstitution der Flavone," *Travaux de la Société des Sciences physico-chimiques à l'Université de Charkoff*, 1902; "Ueber das Rutin der Gartenraute," Magister-Dissert. *Arch. d. Pharmacie*, 1904; "Ueber das Robinin," *Arch. d. Pharm.* und *Journal de la Société physico-chimique Russe* (Pétersbourg), 1904; "Ueber Folia Digitalis," *Médecin. Journal*, Charkoff (russisch), 1907; "Ueber das Kämpferol aus dem Robinin," *Travaux de la Société des Sciences phys.-chimiques Charkoff*, 1908; "Ueber die Bestandteile der Früchten von Rhamnus

cathartica" (mit N. Krassovski), *Journal de la Société physico-chimiques Russe* (Pétersbourg), 1908.

P. W. Robertson. W. B. Tuck.
J. Lister. Edward C. Cyril Baly.

F. G. Donnan.

Weizmann, Charles,

57, Birchfields Road, Rusholme, Manchester.

Senior Lecturer in Chemistry in the University of Manchester. Ph.D. Freiburg; D.Sc. Manchester. Author of some twenty papers in the *Journal of Chemical Society* and the *Berichte* on "The Naphthacene-quinones and Allied Compounds."

Harold B. Dixon. Norman Smith.
W. H. Perkin. H. F. Coward.
Arthur Lapworth. R. Robinson.

Wheeler, Richard Vernon,

The Colliery House, Altofts.

Chemist to the "British Coal-Dust Experiments" Committee. D.Sc. University of Manchester. Joint author of following memoirs: "The Combination of Hydrogen and Oxygen in Contact with Heated Surfaces," *Phil. Trans.*, A., 1906; "Slow Oxidation of Methane at Low Temperatures," *J.C.S.*, 1902; Part II., Ditto, 1903; "Combustion of Ethylene," *J.C.S.*, 1904.

Harold B. Dixon. H. F. Coward.
W. H. Perkin. R. Robinson.
J. F. Thorpe. *Arthur Lapworth.*

Williams, Herbert Ernest,

70, Wellington Road, Charlton, Kent.

Analytical and Manufacturing Chemist. Consulting and Analytical Chemist to John Dewrance, Esq., 165, Great Dover Street, and Chief Chemist of the Albion Chemical Company, Riverside, Charlton, Kent. Have also carried out considerable research on the Compounds of Cyanogen and patentee of a process for the Manufacture of Cyanides.

John M. Dougall. Arthur H. Coote.
T. Wilton. *Ernest Scott.*

Wm. Pearce.

Young, Roland Francis,

c/o Taquah Mining and Expn. Co., Tarkwa, Gold Coast.

Chemist and Metallurgist. Attended three years' course at Finsbury Technical College, 1899–1901, obtaining College certificate. Chemist

to Wouldham Cement Co., 1901–03. Assistant Chemist, Gas Light & Coke Co.'s Tar Works, Beckton, 1903–07. Cyanide Asst., Taquah Mining & Expn. Co., 1907–present time. (Acting Cyanide Manager, Abosso G. M. Co., July–December, 1908.)

R. Meldola. R. Lessing.
J. Louis Foucar. F. W. Linch.
W. H. Glover.

The following Certificates have been authorised for presentation to Ballot by the Council under Bye-Law I (3):

Flack, Edmund Victor,

Mayville, Wigtown Road, Green Point.

Government Analyst. Connexion with Analytical Chemistry. Analyst at the Govt. Analytical Laboratory, Cape Town, S. Africa.

George N. Blackshaw.

Muller, John,

Government Analytical Laboratory, Grahamstown, Cape Colony.

Government Analyst, and Public Analyst for Eastern Province of Cape of Good Hope. B.A. of Cape University, 1895. Specialised for nearly six months at request of Government in Agricultural Chemistry in Halle a/S Germany, 1896. Assistant Analyst in Government Analytical Laboratory, Capetown, 1895–1902. Analyst in charge of Government Analytical Laboratory, Grahamstown, Cape Colony, 1902–1909.

Walter D. Severn.

Peixoto, Joãs Cornelio Rodrigues,

52, Rua N.S. Copacabana, Rio de Janeiro, Brazil.

Analytical Chemist. Two years at the Polytechnic School of Rio de Janeiro. Two years at the University of Brussels. Fourteen months at the Institute Meurice of Practical Chemistry, Brussels (Diploma). I desire to keep in touch with recent research work in England.

T. H. Lee.

Tapp, Charles,

Cradock, Cape of Good Hope.

Analytical Chemist. Minor Diploma Pharmaceutical Society of Great Britain. Certificate of the Apothecaries Society, London. Honours in Chemistry, Westminster College, London. Late Assistant

Analyst to Mr. E. G. Hogg, of London. Member South African Pharmaceutical and Chemical Societies.

John Cussons. *A. John Gregory.*
Thos. H. Moore. *P. Skinner Clark.*
J. Fred. Davis. *J. H. Dinwoodie.*

Wright, Joseph Pretty,

883, Burrard Street, Vancouver, British Columbia.

Cement Expert and Tester for the Corporation of the City of Vancouver, British Columbia. Five years as Cement Expert to City of Vancouver. Pharmaceutical Society, England, 1886.

J. O'Sullivan. *John A. Hall.*

R. CLAY AND SONS, LTD., BREAD STREET HILL, E.C., AND BUNGAY, SUFFOLK

[*Issued* 13/12/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 363.

Thursday, December 2nd, 1909, at 8.30 p.m., Professor HAROLD B DIXON, F.R.S., President, in the Chair.

Mr. Stanley Okell was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs.:

Gilbert Grahame Auchinleck, B.Sc., the Department of Agriculture, Grenada, W.I.
Fred Banister, B.Sc., the Grammar School, Doncaster.
Howard Canton, 2, Gloucester Road, Regent's Park, N.W.
Herbert Hillier Hughes, B.Sc., 22, Ranelagh Road, Tottenham, N.
Douglas Wilshin Murch, Selby House, Victoria Road, Wednesbury.
John James Beaumont Rees, B.Sc., Johannesburg College, S. Africa.

A ballot for the election of Fellows was held, and the following were declared duly elected:

A. K. Yegna Narayan Aiyer, M.A.
Jehangir Dhanjishaw Anklesaria.
James Alexander Hadden Armstrong.
Donald William Elsom Barker.
Harold Baron, B.Sc.
Stanley Robert Best, M.Sc.
Hubert Frederick Bottomley.
Henry Shaw Breakspear, B.A.
O. K. H. Burger, Ph.D.
Frank Ward Bury, B.Sc.
William Edward Callister, B.Sc.
William Gordon Carey.
Hardee Chamblis, M.S., Ph.D.
Lakshami Chand, B.A., B.Sc.
James Ferguson Dawson, B.Sc.
Alfred Charles Dunningham, B.Sc.

Edward Charles Edgar, D.Sc.
Alfred Edge.
Frederick Watson Edwards.
Arthur James Ewins, B.Sc.
Edmund Victor Flack.
George Peters Forrester.
Arthur Forshaw, M.Sc.
William Adolf Freymuth.
Otto Fürstenhagen.
George Pomeroy Furneaux, B.A.
Alexander David Gardiner.
Henry Dent Gardner, jun., M.Sc.
Victor John Harding, M.Sc.
Arthur John Harvey.
Robert Douglas Hendry.
Eric John Holmyard.
Benjamin Leech, M.A.
William Cudmore McCullagh Lewis, M.A.
Carl Olof Lundholm.
John Muller, B.A.
Roland Victor Norris, M.Sc.
Joäs Cornelio Rodrigues Peixoto.
Francis Hugh Ping.
Charles Proud.
Walter Ritchings, M.Sc.
Frederic William Robinson, B.Sc.
Pindi Das Sabherwal.
Manindra Sinha.
Spencer Boyd Oortis-Stanford.
Guy Stephenson.
George Bertram Stones, M.Sc.
James Thallon Strachan.
Edward Walter Taplin.
Charles Tapp.
Hermann Thoms, Ph.D.
Joseph Grantley Tingle.
Henry Thomas Tizard, B.A.
Herbert Turner, B.Sc.
Everard Cecil Van Essen.
Nikolai Waliaschko.
Charles Weizmann, D.Sc., Ph.D.
Richard Vernon Wheeler, D.Sc.
Herbert Ernest Williams.
Joseph Pretty Wright.
Roland Francis Young.

Of the following papers, those marked * were read:

***270. "A new method for the detection of sodium, cæsium, and rubidium." By Walter Craven Ball.**

A solution of potassium bismuth nitrite, to which about 1 per cent. of cæsium nitrate has been added, produces a yellow, crystalline precipitate of $9CsNO_2,6NaNO_2,5Bi(NO_2)_3$, with traces of a sodium salt. One part of sodium in presence of several thousands of potassium may thus be detected. Conversely, a solution of sodium bismuth nitrite is an excellent test for cæsium, and also for rubidium, if in not too great dilution.

Discussion.

Mr. Grant Hooper said that the author had referred to the precipitate which was thrown down when the reagent was exposed to oxidation by contact with the air, and, in connexion with the quantitative determination of sodium, he desired to ask how this precipitate from the reagent was affected by the 50 per cent. acetone which was used to wash the sodium compound. It appeared as if there was some danger of the sodium, as determined under these conditions, coming out too high, and he observed that the last determination quoted by the author was, in fact, a trifle high.

***271. "Note on Dr. Scott's paper on the molecular weight of tetraethylammonium bromide and the atomic weight of carbon." By Sir Edward Thorpe, C.B.**

In determinations of atomic weight when the utmost attainable precision is aimed at, it is customary to reduce the weighings to what is styled a vacuum standard, and the reduction is almost invariably made by a calculation in which the relative densities of air, of the weights, and of the substance weighed are the data.

Marignac, as far back as 1843, pointed out that in certain cases, more particularly when the substance weighed was in a fine state of sub-division, this method might be attended with error, due to the tendency of finely-divided substances to occlude and condense air.

In a recent paper (*Compt. rend.*, 1909, **149**, 593), Guye and Zachariades have again drawn attention to this circumstance. They state that with certain substances the error may be so considerable as to affect materially the determination of the value of an atomic weight. By weighing successively in air and in a vacuum, the same mass of finely-divided material (from 20 to 50 grams, depending on its density), and comparing the weight so obtained with that deduced by the conventional method of calculation, they found that the method of calculation invariably over-corrects the weight, and that the difference between the weight actually observed and that obtained by calculation may amount to as much as, or even more than, $\frac{3}{10,000}$

The extent of the difference appears to depend on several factors. In the first place, it depends on the density of the salt, salts of low specific gravity always tending to show the greatest variation. But it also depends, and in a greater degree, on the physical state of the salt. Thus in the case of fused potassium chloride (sp. gr. 1·97) the difference shown by the salt in powder was 32 milligrams per 100 grams; in crystals it was 20 milligrams; in large pieces it was only 5 milligrams. In the case of fused masses of salts of high density, and in that of fused metals, the discrepancy, if observed, is extremely small, and in such cases is practically negligible.

In a recent communication to the Society (*Trans.*, 1909, **95**, 1200), Dr. Scott has given the results of a number of determinations of the molecular weight of tetraethylammonium bromide, from which he has deduced an atomic weight for carbon slightly in excess of that obtained by the combustion of carbon, of graphite, of pure charcoal, and that deduced by physico-chemical methods, all of which agree extremely well among themselves and consistently point to the value C = 12·00.

The author believes the discrepancy observed by Dr. Scott may be

largely, if not altogether, accounted for by the circumstance first pointed out by Marignac. Tetraethylammonium bromide is a salt of very low specific gravity (in a private communication Dr. Scott informed the author that he found it to be 1·35), and, as he mentions in his paper, it was employed by him in the state of a fine powder. Tetraethylammonium bromide is not included in the long list of substances experimented upon by Guye and Zachariades, and no direct data exist for determining the precise value of the correction to be applied to its so-called vacuum weight. There is, in fact, no substance in the list of so low a specific gravity as 1·35, but considering the nature of the salt it is reasonably certain that it must be as great as, and in all probability greater than, the maximum value hitherto found. The maximum value obtained by Guye and Zachariades was observed in the case of potassium nitrate (sp. gr. 2·09), namely, 33 milligrams per 100 grams.

To ascertain what might be the influence of Marignac's correction in the case of Dr. Scott's observation, this value of 33 milligrams may be applied. Dr. Scott found that, collectively, 44·17031 grams of tetraethylammonium bromide were equivalent to 22·66675 grams of silver. Applying Guye and Zachariades' number, the aggregate weight of the tetraethylammonium bromide would probably be at most 44·15573 grams, and on the assumption that the atomic weight of silver is 107·88, this would give the molecular weight of the salt as 210·154.

Taking the molecular weight of ammonium bromide as 97·962, on the basis of what is the accumulated testimony of the best determinations of the several atomic weights of its elements, we obtain 112·192 as the molecular weight of C_8H_{16}, whence we have C = 12·008.

It cannot, therefore, be regarded as established that the weight of the carbon atom in tetraethylammonium bromide, or in the group C_8H_{16}, is different from what it has been found to be in other carbon compounds.

The slight variation which Dr. Scott has observed will, in the author's opinion, be proved to be mainly, if not entirely, dependent upon the physical peculiarities of the salts he has employed.

***272. "The correction of weights of substances weighed in air to weights in a vacuum." By Alexander Scott.**

Before passing to the consideration of the work of Marignac and of Guye and Zachariades with reference to corrections to vacuum standards, whether by experiment or by calculation in the ordinary way, the author referred to the note on his determination of the atomic weight of carbon by Sir Edward Thorpe (preceding paper). One point

especially emphasised was that the value for C_8H_{16} is based on the difference between the molecular weights of tetraethylammonium bromide and ammonium bromide, both values being determined in the same way, with the same balance, pure silver, and the same set of carefully calibrated weights. It was thus hoped to eliminate any sources of error which might possibly be due either to the method or to personal equation. Therefore, if it is fair to deduct 33 milligrams per 100 grams of tetraethylammonium bromide, as Sir Edward has done, it would only be fair to take at least 22 milligrams from 100 grams of ammonium bromide, which would make for the 97·950 grams, which are equivalent to 107·88 of silver, 97·928 to be subtracted from Sir Edward Thorpe's calculated value of 210·154, and this gives C = 12·013 (taking H = 1·0075). Furthermore, a similar correction ought to be applied to the combustion of carbon, for if any substance is capable of condensing air in its pores it is carbon. Applying the correction of 33 milligrams per 100 grams to the careful experiments of van der Plaats, with sugar and paper charcoal, we get instead of C = 12·004, C = 11·998, so that the final effect of applying this correction all round is to increase rather than diminish the difference in the atomic weight of carbon as found by combustion methods and by the author's method.

As pointed out by Sir Edward Thorpe, Marignac (*Bibl. Univ.*, 1843, **46**, 373) stated that there was a slight difference in the value of the correction to vacuum standards as found by the usual method of calculation from a knowledge of the densities of the substances involved and that found by direct weighing of these substances in a vacuum. This, however, is only very slight, as the following table shows. The author has added the last three columns to Marignac's table, taking the best values for the mean densities of the salts, and Marignac's value of 1·2 milligrams for 1 c.c. of air.

Salt.	Weight in air.	Weight in a vacuum.	Weight of equal volume of air.	Density.	Error in milligrams.
$AgClO_3$	100	100·029	0·027	4·43	−2·0
$AgBrO_3$	100	100·021	0·023	5·21	+2·0
$KClO_3$	100	100·054	0·0515	2·33	−2·5
$KBrO_3$	100	100·044	0·0373	3·22	−6·7
KIO_3	100	100·030	0·308	3·89	+0·8
NH_4Cl	100	100·080	0·0792	1·515	−0·8

As Marignac's weighings are only given to milligrams, presumably his balance was only sensible to a milligram, and an examination of the last columns shows, with the one exception of potassium bromate, that the evidence is quite as much against as in favour of his statement that any sensible error exists.

The recent paper of Guye and Zachariades (*Compt. rend.*, 1909, **149**, 593) gives a list of twenty-six substances, with their densities, and

the errors stated to occur when 100 grams of each are weighed in air in fine powder and the correction for the displaced air applied in the usual way. This error they, like Marignac, ascribe to air condensed in the pores of the fine powders, although it is difficult to see why "*hygroscopicité*," as stated in their paper, should also enter into the question. These errors range from 33 milligrams in the case of potassium nitrate to only 1 for copper oxide. For potassium chloride they give more data, stating that the errors are 5 milligrams for fused lumps, 22 for crystals, and 32 milligrams for fine powder. This last number means that 32 milligrams, or 27 c.c. of air, are condensed in the pores of 100 grams of finely-powdered potassium chloride, and therefore ought to be evolved with effervescence when the latter is dissolved in ordinary distilled water.

This statement seemed so extraordinary that the author weighed in a vacuum and in air potassium chloride in fused lumps, in crystals, and in fine powder, and observed practically no difference between the weights referred to a vacuum, whether found directly or by the ordinary method of calculation, with this precaution, however, that the calculation was made with the actual density of the air as determined at the time and not an average density as is too often done. The slight differences, which still seem to remain, would be in all probability completely removed had time permitted the preparation of an exact counterpoise to the vessel used to contain the salt. As, however, all this work has been carried out since Sir Edward Thorpe had most courteously sent the author a copy of the note communicated by him to the Society, it has not been possible to employ all the refinements which modern science suggests. The apparatus employed was a large test-tube, with cap carefully ground, and to which was sealed a good glass stopcock, both capable of keeping a vacuum for days, and a small flask similarly fitted. Their volumes were respectively 186·5 and 82·16 c.c. The large tube had to be weighed on a larger and less sensitive balance than the small flask.

	Fused salt.	Salt in crystals.	Salt in fine powder.
Weight of tube, vacuous	101·2616	101·2472	39·0418
,, ,, full of air	101·4876	101·4684	39·1424
,, ,, +KCl	215·5280	202·9178	106·8062
,, ,, +KCl+air	215·6840	203·0776	106·8648
,, KCl in a vacuum	114·2664	101·6706	67·7644
,, ,, in air	114·1964	101·6092	67·7224
,, air displaced	0·0700	0·0614	0·0420
,, air along with KCl	0·1560	0·1598	0·0586
,, total air	0·2260	0·2212	0·1006
,, 1 c.c. of air in milligrams	1·212	1·186	1·23
Calculated correction for air	0·0703	0·0617	0·0423
Density of substance	1·9698	1·9527	1·9702
Error	0·0003	0·0003	0·0003

In addition to the three experiments of which the results are given in the preceding table, two other experiments with crystals and fine powder were made with like results.

Mr. J. D. Kettle, chief assistant at the Davy-Faraday Laboratory, took finely-powdered benzoic acid (a less dense substance than any of the substances mentioned above), and, on fusing 19·8 grams of it in a vacuum and using a tube of approximately the same weight and volume as a counterpoise, was unable on a still more sensitive balance to detect the slightest change in weight, and no trace of gas was given off on fusion which could be detected by a mercury gauge any more than by the balance; as some of the salts in Guye and Zachariades' list were apparently hydrated, perhaps some of their results may have been due to loss of water, otherwise no explanation can be given of their most remarkable results. Until a detailed account of their work, giving the actual weighings, is available, further criticism is hardly called for.

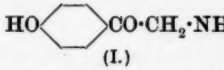
***273. "Synthesis of hordenine, the alkaloid from barley." By George Barger.**

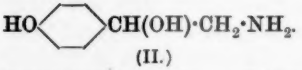
Hordenine, isolated by Léger (*Compt. rend.*, 1906, **142**, 108) from barley germs, and recognised by him as *p*-hydroxyphenylethyldimethylamine, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, has now been synthesised from phenylethyl alcohol, which was successively converted into *β*-phenylethyl chloride and phenylethyldimethylamine; the phenolic hydroxyl was then introduced by successive nitration, reduction, and diazotisation.

The more obvious synthesis, by methylation of *p*-hydroxyphenylethylamine (Barger, *Trans.*, 1909, **95**, 1123), could not be carried out; by this means only hordenine methiodide was obtainable, but not hordenine itself.

***274. "Syntheses in the epinephrine series." By Frank Tutin, Frederic William Caton, and Archie Cecil Osborn Hann.**

The authors have prepared *ω-amino*-p-*hydroxyacetophenone* (I) and *β*-p-*dihydroxy-β-phenylethylamine* (II).


(I.)


(II.)

Both of these compounds, when injected intravenously, considerably increase the blood-pressure. The latter compound, however, is the more powerful, and, in its action, more closely resembles epinephrine.

The formation and properties of the above-mentioned bases (I and II) and of a number of other new compounds were described.

275. "The correction of the specific gravity of liquids for the buoyancy of air." By John Wade and Richard William Merriman.

In determining the specific gravity of liquids to the fifth decimal place, neglect of variations in atmospheric density may lead to serious error, more especially when the water-content of the pyknometer is not determined under the same atmospheric conditions as those obtaining at the time of weighing the liquid. Analysis of the limits of accuracy of the customary correction formula leads to some simple expressions which, with the aid of tabulated constants, materially reduce the labour of correction.

276. "Syntheses with the aid of monochloromethyl ether. Part II. The action of monochloromethyl ether on the sodium derivative of ethyl acetoacetate." By John Lionel Simonsen and Robert Storey.

The authors showed that monochloromethyl ether and ethyl sodioacetoacetate condense with the formation of *ethyl methoxy-β-methoxycrotonate* and ethyl αγ-diacetylglutarate.

277. "The relation between the chemical constitution of monazo-dyes and their fastness to light." By Edwin Roy Watson, A. Chandra Sirkar, and Jatindra M. Dutta.

From rules which had been already formulated by one of the authors (this vol., p. 224) it was expected that the dyes sulphobenzeneazophenolmonosulphonic acid and sulphobenzeneazophenoldisulphonic acid would be very fast to light. This was found to be the case. Sulphobenzeneazophenol was also found to be very fast to light. Contrary to the usual assumption that a hydroxy- or amino-group must be present in an azo-compound to give it dyeing properties, it was found that azobenzenedisulphonic acid is a dye, and, owing to the presence of sulphonic groups and the absence of any hydroxy- or amino-group, it was found to be very fast to light.

It was predicted that phenol would be formed as one of the decomposition products when chrysoidine faded in light, and when this was put to the test phenol was found.

It was also predicted that the introduction of bromine atoms or a nitro-group into the phenolic or arylamino-part of a monazo-dye would increase its fastness to light, and that the fastness to light of amino-azobenzene would depend on the position of the amino-group, *m*-amino-

azobenzene being faster than *p*-aminoazobenzene. The fastness to light of the following dyes was compared: aminoazobenzene, benzeneazodibromoaniline; benzeneazophenol, benzeneazonitrophenol; sulphobenzeneazophenol, sulphobenzeneazonitrophenol; *p*-aminoazobenzene, *m*-aminoazobenzene, and *o*-aminoazotoluene. The theory, on which these predictions were based, as to the manner of fading of azo-dyes in light was not confirmed by this investigation to the extent anticipated.

278. "The triazo-group. Part X. Triazoantipyrine." By Martin Onslow Forster and Robert Müller.

The preparation and properties of triazoantipyrine were described, and attention was drawn to the behaviour which distinguishes it from other triazo-ketones.

279. "Volumetric estimation of sulphates." By Alec Duncan Mitchell and Clarence Smith.

The method consists essentially of adding a small excess of $2N/5$-barium chloride solution, destroying mineral acid by sodium acetate, adding excess of $N/10$-ammonium dichromate solution, and making up to 100 c.c.; when the precipitate has settled, 25 c.c. of the clear supernatant liquid are titrated with $N/20$-ferrous ammonium sulphate solution, using potassium ferricyanide as an external indicator.

This has been applied to ammonium sulphate, sodium sulphate, potassium sulphate, zinc sulphate, magnesium sulphate, and copper ammonium sulphate, and gives results accurate to about 0·2 per cent., although in the case of potassium sulphate special precautions have to be adopted to minimise adsorption. Excluding weighings, five determinations may easily be made in a hour.

280. "The colouring matter of cotton flowers. Gossypium herbaceum. Part II." By Arthur George Perkin.

The flowers of the Egyptian cotton plant, a variety of the *Gossypium herbaceum*, have been found to contain three hitherto unknown glucosides. *Quercimeritrin*, $C_{21}H_{20}O_{12}$, the main constituent, crystallises with $3H_2O$ in small, yellow plates, m. p. 247—249°, dyes mordanted fabrics very similarly to quercetin, and gives with lead acetate an orange-red precipitate. It forms an *octa-acetyl* compound, $C_{21}H_{12}O_{12}(C_2H_3O)_8$, colourless needles, m. p. 214—216°, and is hydrolysed with difficulty according to the equation:

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$$

into quercetin and dextrose (osazone, m. p. 204—205°). iso*Quercitrin*, $C_{21}H_{20}O_{12}$ (dried at 160°), consists of pale yellow needles, m. p. 217—219°, and is readily hydrolysed by acid:

$$C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$$

with formation of quercetin and dextrose, but differs from quercimeritrin in several important respects. With lead acetate it gives a bright yellow precipitate, dyes mordanted fabrics similarly to quercitrin (*Trans.*, 1902, **81**, 480), and is present in the flowers in small amount. The third glucoside, *gossypitrin*, $C_{21}H_{20}O_{13}$ (dried at 160°), pale orange-yellow needles, m. p. about 200—202°, when hydrolysed gives gossypetin and dextrose:

$$C_{21}H_{20}O_{13} + H_2O = C_{15}H_{10}O_8 + C_6H_{12}O_6.$$

It yields a bright red precipitate with lead acetate, and dyes mordanted fabrics. The flowers yielded 1·86 per cent. of yellow colouring matter, consisting of quercetin mixed with about 10 per cent. of gossypetin.

281. "Viscosity and association in binary mixtures of liquids." By George Senter.

In a recent paper (*Trans.*, 1909, **95**, 1556) dealing with the viscosity of binary mixtures of liquids, Dunstan and Thole state that the maxima observed in certain viscosity-concentration curves of such systems "invariably occur at or near points of simple molecular composition," and are connected with the formation of definite chemical compounds between the components of the mixture. In this connexion they refer to the brief discussion of this subject in the author's *Outlines of Physical Chemistry* (p. 305—306), in which it is stated that no general agreement has yet been reached with reference to the interpretation of such curves, and they suggest that the considerations there advanced present no obstacle to the general acceptance of the association explanation of the phenomenon.

The experimental work described by Dunstan and Thole was undertaken with the object of throwing light on the displacement of the maxima with temperature, but, unfortunately, observations have only been made over a range of 10° (20—30°), which is too small to allow of any very definite conclusions being drawn. However, it is known from the observations of Arrhenius, quoted in the paper, that in mixtures of ethyl alcohol and water, the viscosity maximum at 0° occurs at a composition of 36 per cent. of alcohol and at 55° at 50 per cent. of alcohol, so that there is an undoubted shift of the maximum with temperature in this case, and doubtless in other cases.

Dunstan and Thole now maintain that such a shift of the maximum does not disprove the association explanation of this phenomenon, and with this the author agrees. It does, however, entirely disprove the suggestion that such maxima invariably occur "at" points of simple molecular composition, since the position of the maximum in the case cited alters continuously with rise of temperature through a wide range of concentration. The qualifying word "near" does not seem to have any well-defined meaning in the present case, as a mixture of two components in any proportions whatever may be looked upon as being "near" a point of simple molecular composition.

Even if the association explanation of the maxima be accepted, it is improbable that the observations throw any light on the composition of the compounds unless the latter are exceptionally stable, like $H_2SO_4(H_2O,SO_3)$ and H_2SO_4,H_2O. In this connexion it is suggestive to note that, according to Kremann (*Monatsh.*, 1907, **28**, 831), the viscosity curve of the system *m*-cresol-aniline, at 0°, shows a maximum at 85 mol. per cent. of the former, although the components only form one compound, containing one molecule of each. Similarly, the viscosity curve of the system phenol-aniline shows a maximum at 67 mol. per cent. of phenol, although only one compound is known containing the components in molecular proportions.

The numerous investigations on alloys carried out in recent years appear to throw some light on this question. According to Tammann (*Zeitsch. anorg. Chem.*, 1907, **53**, 446), it is a general rule that metals belonging to the same natural group form solid solutions (mixed crystals), but no chemical compounds. Now Kurnakoff and Schemtschuschny (*Zeitsch. anorg. Chem.*, 1908, **60**, 1) have shown with reference to the hardness of binary systems (a property allied to viscosity) (1) that the hardness of an unbroken series of solid solutions is often represented by a continuous curve showing a maximum; (2) that a chemical compound may be harder or softer than either of the components. It is not improbable that similar rules may apply to the viscosity of liquid mixtures. There does not seem to be any reason to assume a priori that the viscosity of a compound must be greater than that of its components, especially if the latter are themselves associated.

With reference to the two systems showing maxima specially dealt with in the paper by Dunstan and Thole, cited above, it may be noted that the freezing-point curve of mixtures of acetic acid and water shows no indications of the presence of a compound (Kremann, *Monatsh.*, 1907, **28**, 893), although the observations were made at a lower temperature than the viscosity measurements described in the paper. Moreover, Jones (*Zeitsch. physikal. Chem.*, 1894, **13**, 419) has shown that mixtures of ethyl alcohol and water exert their effect on

the freezing point of acetic acid quite independently; he thus obtained no evidence of combination between the first two compounds, although the corresponding experiments with mixtures of sulphuric acid and water showed quite conclusively the formation of compounds.

The fact that the maxima on the viscosity curves become less distinct the higher the temperature does not appear very conclusive from the point of view of association, as it is a rule of very wide applicability that the simple laws (in this case, the mixture law) are followed the more closely the higher the temperature.

Among the factors which have to be taken into account in discussing the properties of binary systems are to be considered, besides possible chemical combination, alterations in molecular complexity and attractions between the molecules (analogous to the a/v^2 term of van der Waals' equation) connected with alterations of "internal pressure" (compare Tammann, *Innere Kräfte und Eigenschaften der Lösungen*, Leipzig, 1907). These factors may be more or less connected, but, on the other hand, the existence of unimolecular liquids indicates that there may be considerable attraction (measured by the term a/v^2) between molecules without leading to chemical combination.

The general conclusion is that at present there are no means of reaching a definite decision on this matter, and we have to depend on rather uncertain criteria which do not all point in the same direction.

282. "Preparation of anhydrides by the action of thionyl chloride on salts of organic acids." (Preliminary note.) By William Smith Denham.

The author has shown (*Trans.*, 1909, **95**, 1235) that sulphur monochloride acts readily on the sodium or silver salts of organic acids in presence of indifferent solvents, forming unstable sulphur compounds of the type $(R\cdot CO_2)_2S_2$, which, on spontaneous decomposition, give anhydrides of the acids, together with sulphur dioxide and sulphur.

Since, according to one view, thionyl chloride has a constitution similar to that of sulphur monochloride, attempts have now been made to obtain compounds of the type $(R\cdot CO_2)_2SO$ by the substitution of thionyl chloride in the above reaction. Intermediate compounds of this type were not obtained, but it was found that reaction takes place smoothly and readily between typical silver salts and thionyl chloride, with evolution of sulphur dioxide and formation of the acid anhydride, probably according to the equation: $2R\cdot CO_2Ag + SOCl_2 = (R\cdot CO)_2O + SO_2 + AgCl$. As in this case sulphur dioxide is the only product in addition to the anhydride, this modification of the reaction possesses obvious advantages as a method of preparing anhydrides

over that in which sulphur chloride is used. The reaction is carried out as described in the case of sulphur chloride, that is, by adding thionyl chloride dissolved in dry ether to a slight excess of the silver salt suspended in the same solvent, the containing vessel being cooled if necessary. After filtration from silver chloride and distillation of the ether, the anhydride is left in good yield, and generally nearly pure. In this way, acetic, benzoic, and succinic anhydrides have already been obtained.

Whilst sulphur chloride does not, under these conditions, react with silver oxalate or with silver malonate, thionyl chloride does react, but only decomposition products have been obtained.

The author proposes to apply this method to the preparation of anhydrides of hydroxy-acids and of optically active acids, and to the preparation of mixed anhydrides. Preliminary experiments indicate that this may be successfully done, and the author made this preliminary announcement in view of the fact that H. Meyer (*Chem. Zeit.*, 1909, **33**, 1036) outlines a method of preparing anhydrides of sulphonic acids from the corresponding alkali salts by the action of thionyl chloride.

283. "A new synthesis of oxazole derivatives." By Robert Robinson.

The author has found that certain acyl derivatives of ω-aminoacetophenone are condensed, under the influence of sulphuric acid, to oxazoles.

ω-Benzoylaminoacetophenone, prepared by benzoylating ω-aminoacetophenone, crystallises in needles, melting at 123°, and when warmed with sulphuric acid furnishes 2 : 5-diphenyloxazole (E. Fischer, *Ber.*, 1896, **29**, 207). *ω-Phenylacetylaminoacetophenone* is obtained by the action of phenylacetyl chloride on ω-aminoacetophenone stannichloride in the presence of potassium hydroxide; it forms colourless needles or prisms melting at 104°. The *oxime* melts at 154°, and the *phenylhydrazone* at 184—185°.

When ω-phenylacetylaminoacetophenone is dissolved in sulphuric acid, it gives rise to *5-phenyl-2-benzyloxazole*, crystallising in long, flat needles melting at 89°; the *picrate* melts at 103°. *α-Hydroxy-β-phenylacetylamino-α-phenylethane*, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$, prepared by reducing ω-phenylacetylaminoacetophenone with sodium and dilute methyl alcohol, forms colourless prisms melting at 99°; it does not condense to an oxazole. On warming ω-benzoylaminoacetoveratrone with sulphuric acid, *2-phenyl-5-veratryloxazole* is obtained in slender needles melting at 97°, and, in a similar manner, *2-benzyl-5-veratryloxazole*, colourless needles, melting at 86°, is obtained from

ω-phenylacetylaminoacetoveratrone, which melts at 135°, and is prepared from ω-aminoacetoveratrone stannichloride and phenylacetyl chloride. Reduction of 2-oximino-5 : 6-dimethoxy-1-hydrindone and benzoylation of the *hydrochloride* of the resulting 2-*amino*-compound furnishes 2-*benzoylamino*-5 : 6-*dimethoxy*-1-*hydrindone*, which crystallises in needles melting at 224°; the compound does not condense to an oxazole under the influence of sulphuric acid.

284. "Ethyl benzoylacetate."
By Edward Hope and William Henry Perkin, jun.

The authors have made a careful investigation of the conditions under which ethyl benzoylacetate is converted into mono- and di-substitution derivatives, and of the behaviour of these on hydrolysis.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Cook, *John.* Clavis Naturæ: or, the mystery of philosophy unvail'd. pp. xiv + 405. London 1733. From Mr. C. H. Cribb.

Iron and Steel Institute. Carnegie Scholarship Memoirs. Vol. I. pp. xii + 368. ill. London 1909. From the Institute.

II. *By Purchase.*

Laubenheimer, *Kurt.* Phenol und seine Derivate als Desinfektionsmittel. pp. vi + 156. Berlin 1909. (*Recd.* 24/11/09.)

Loeb, *Jacques.* Die chemische Entwicklungserregung des tierischen Eies. (Künstliche Parthenogenese.) pp. xxiv + 259. ill. Berlin 1909. (*Recd.* 24/11/09.)

Moser, *L.* Die Bestimmungsmethoden des Wismuts und seine Trennung von den anderen Elementen. (Die chemische Analyse, Vol. X.) Stuttgart 1909.

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Oppenheimer, *Carl.* Die Fermente und ihre Wirkungen. Spezieller Teil. 3rd edition. pp. xi + 491. Leipzig 1909. (*Recd.* 24/11/09.)

Ostwald, *Wolfgang.* Grundriss der Kolloidchemie. pp. xiv + 525. Dresden 1909. (*Recd.* 24/11/09.)

Starling, *Ernest H.* The Mercers' Company Lectures on the fluids of the body. pp. viii + 186. London 1909. (*Recd.* 27/11/09.)

Zerr, *George,* and **Rübencamp,** *R.* A treatise of colour manufacture. A guide to the preparation, examination, and application of all the pigment colours in practical use. Authorised English edition by *Charles* **Mayer.** pp. xiii + 605. ill. London 1908. (*Recd.* 27/11/09.)

III. *Pamphlets.*

Aschan, *Ossian.* Ueber die Konstitution des Isopinens. (From the *Öfversigt Finska Vetensk. Soc. Förhandl.*, 1908–1909, **51**, *A.*)

Barger, *George,* and **Dale,** *Henry Hallett.* The water-soluble active principles of ergot. (From the *J. Physiol.*, 1909, **38**.)

Barger, *George,* and **Walpole,** *George Stanley.* Isolation of the pressor principles of putrid meat. (From the *J. Physiol.*, 1909, **38**.)

Dale, *Henry Hallett.* Note on nutmeg-poisoning. (From the *Proc. Roy. Soc. Med.*, 1909.)

Dale, *Henry Hallett,* and **Dixon,** *Walter Ernest.* The action of pressor amines produced by putrefaction. (From the *J. Physiol.*, 1909, **39**.)

Goerner, *Paul.* Aromatische Nitroderivate insbesondere Nitrophenole als Alkaloidfaellungsmittel. pp. 45. Strassburg 1908.

Nebraska, University of. *Agricultural Experiment Station.* Twenty-second annual report. pp. 158. ill. Lincoln, Nebraska, 1909.

Neubauer, *Otto.* Ueber den Abbau der Aminosäuren in gesunden und kranken Organismus. (From the *Deut. Archiv. klin. Med.*, 1909, **95**.)

Palladino, *Pietro.* Du poids absolu des corps élémentaires et dépendance de leurs propriétés chimiques et physiques du poids absolu et de la forme. pp. 44. ill. Genova 1909.

Pfyl, *B.*, and **Rasenack,** *P.* Ueber die Verpuffungs und Verbrennungsprodukte von Zelluloid. (From the *Arbeiten K. Gesundheitsamte*, 1909, **32**.)

Rusconi, *Arnaldo.* Ricerca dell' alcool etilico nel cloroformio. (From the *Arch. Farmacol. sper. Sci. affini*, 1909, **8**.)

Zimmerman, *Joseph.* Ueber die Spaltung des Gypsophila-Saponins. pp. 58. Strassburg 1909.

JULIUS THOMSEN MEMORIAL LECTURE.

The Julius Thomsen Memorial Lecture will be delivered by Professor Sir EDWARD THORPE, C.B., F.R.S., at the Ordinary Scientific Meeting on Thursday, February 17th, 1910, at 8.30 p.m.

At the next Ordinary Scientific Meeting on **Thursday, December 16th, 1909, at 8.30** p.m., the following papers will be communicated:

"The production of para-diazoimides from alkyl- and aryl-sulphonyl-para-diamines. A general reaction." By G. T. Morgan and J. A. Pickard.

"Organic derivatives of antimony. Part I. Tricamphorylstibine chloride and triphenylstibine hydroxynitrate and hydroxysulphate." By G. T. Morgan, Miss F. M. G. Micklethwait, and G. S. Whitby.

"The constituents of *Rumex ecklonianus*." By F. Tutin and H. W. B. Clewer.

"The influence of non-electrolytes on the solubility of carbon dioxide in water." By F. L. Usher.

"Ethyl hydroxy*iso*butyrate." By W. Parry.

"The condensation of benzaldehyde with resorcinol." By F. G. Pope and H. Howard.

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[*Issued* 30/12/09

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 25. No. 364.

Thursday, December 16th, 1909, at 8.30 p.m., Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

Referring to the loss sustained by the Society in the death of Dr. Ludwig Mond, the PRESIDENT stated that the Council had that afternoon passed the following resolution: "The Council of the Chemical Society desire to place on record their profound regret at the death of Dr. Ludwig Mond—a man distinguished no less for his life-long researches in pure and applied Chemistry than for his wise beneficence for the advancement of Science. Dr. Mond was elected a Fellow of this Society in 1872, and served as a member of Council in 1885–6 and as Vice-President from 1887 to 1890, and again from 1894 to 1898. In the present year he was invited by the Council to accept nomination for the Presidency: unfortunately, ill-health prevented his acceptance. The industrial processes which Dr. Mond established and gradually perfected presented chemical and engineering problems only to be solved by a rare combination of scientific insight and of practical skill. The faith of Dr. Mond in well-guided research as the fertiliser at the root of a nation's industry was shown again and again when he applied his wealth to aid original investigation. Among his generous benefactions to the cause he had at heart, two stand out conspicuously—the fund which enabled the Royal Society to publish its catalogue of scientific papers, and the creation and endowment of the splendid Davy-Faraday Research Laboratory. To his adopted country Dr. Mond's work has been a help and an inspiration; we, his

Chemical colleagues, who know what that work was, desire to convey to his family our sense of the loss that science and the country have sustained."

It was further announced by the PRESIDENT that in view of the completion of fifty years' Fellowship by the Past Presidents the Rt. Hon. Sir Henry Roscoe, Sir William Crookes, Dr. Hugo Müller, and Dr. A. Vernon Harcourt, it has been resolved by the Council that the Society hold a dinner some time at the end of May or beginning of June, 1910, and that these gentlemen be entertained as guests of the Society.

Mr. Harold Baron was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs.:

Percival Frederick Adams, 81, Rock Avenue, Gillingham.
Alexander Charles Cumming, D.Sc., 39, Viewforth, Edinburgh.
Arthur Ernest Everest, B.Sc., Clifton House, Shrewsbury.
Aquila Forster, B.Sc., 156, Coatsworth Road, Gateshead-on-Tyne.
Charles Wright Meanwell, 15, Woodlands Crescent, Muswell Hill, N.

Certificates have been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of Messrs.:

Tarak Nath Das, B.Sc., 31, Bhaironath, Benares City, India.
John William McBeath, West End, Kimberley, S. Africa.

Of the following papers, those marked * were read:

*285. "The production of para-diazoimides from alkyl- and arylsulphonyl-para-diamines. A general reaction." By Gilbert T. Morgan and Joseph Allen Pickard.

Earlier experiments having shown that many arylsulphonyl-*p*-diamines yield arylsulphonyl-*p*-diazoimides on treating their diazonium salts with aqueous sodium acetate, a further selection of these acylated diamines containing very dissimilar alkyl- and aryl-sulphonyl groups has been examined, with the result that this condensation has been found to be a general one.

Benzene-1 : 3 : 5-*trisulphonyltri*-p-*phenylenediamine*,

$$C_6H_3(SO_2\cdot NH\cdot C_6H_4\cdot NH_2)_3,$$

was taken as a typical example of a *p*-aminophenylamide derived from an aromatic polysulphonic acid. When successively diazotised and treated with aqueous sodium acetate, it gives rise to the complex *p*-diazoimide, *benzene*-1 : 3 : 5-*trisulphonyltri*-p-*phenylenediazoimide*,

$$C_6H_3(SO_2\cdot N\cdot C_6H_4\cdot N_2)_3.$$

As a type of a diamine containing a mixed aromatic alkylsulphonyl group, *toluene-ω-sulphonyl*-p-*phenylenediamine*,

$$C_6H_5\cdot CH_2\cdot SO_2\cdot NH\cdot C_6H_4\cdot NH_2,$$

was prepared; it readily yields *toluene-ω-sulphonyl*-p-*phenylenediazoimide*, $C_6H_5\cdot CH_2\cdot SO_2\cdot N{<}\begin{smallmatrix}C_6H_4\\|\\N_2\end{smallmatrix}$.

The general character of this condensation was finally demonstrated by preparing the two simplest members of the series of alkylsulphonyl-*p*-diazoimides, namely, *methanesulphonyl*-p-*phenylenediazoimide*,

$$CH_3\cdot SO_2\cdot N{<}\begin{smallmatrix}C_6H_4\\|\\N_2\end{smallmatrix},$$

and *methanedisulphonylbis*-p-*phenylenediazoimide*,

$$CH_2(SO_2\cdot N{<}\begin{smallmatrix}C_6H_4\\|\\N_2\end{smallmatrix})_2,$$

obtained respectively from *methanesulphonyl*-p-*phenylenediamine*,

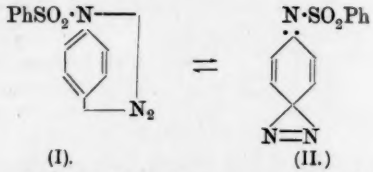
$$CH_3\cdot SO_2\cdot NH\cdot C_6H_4\cdot NH_2,$$

and *methanedisulphonylbis*-p-*phenylenediamine*,

$$CH_2(SO_2\cdot NH\cdot C_6H_4\cdot NH_2)_2.$$

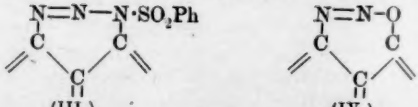
Discussion.

Dr. Morgan, in reference to Prof. Armstrong's expression of opinion that the para-diazoimides were equilibrated mixtures, said that he should be inclined to regard this series, and also the closely allied para-diazo-oxides, as having alternately para-cyclic and para-quinonoid structures:



(I). (II.)

were it not for the fact that these compounds closely resemble in physical and chemical properties the naphthylene-1 : 8-diazoimides (III) and 1 : 8-diazo-oxides (IV) respectively. In the absence of evidence concerning the properties of peri-(1 : 8)-naphthaquinone or its derivatives, it seems preferable to regard these 1 : 8-naphthylene-diazoimides and diazo-oxides as being cyclic compounds with 6-membered rings (III and IV), and thence by analogy to accept formula (I) as representing the structure of the para-diazoimides.



(III.) (IV.)

In answer to Dr. Hewitt's question as to the constitution of non-aromatic diazonium salts, he was of opinion that so long as one of the three phases of the diazonium oscillation could be formulated, the existence of the diazonium salt was possible, although such a compound with only one phase would be less stable than the aromatic diazonium salt with three phases. The dynamic hypothesis of the constitution of diazonium salts would be overthrown by the diazotisation of an amino-derivative of a fully saturated organic complex, but this result had never yet been realised experimentally.

***286. "Organic derivatives of antimony. Part I. Tricamphorylstibine chloride and triphenylstibine hydroxynitrate and hydroxysulphate." By Gilbert T. Morgan, Frances M. G. Micklethwait, and George Stafford Whitby.**

Comparative experiments on the interaction of sodium camphor and the trichlorides of phosphorus, arsenic, and antimony have shown that, in the last case, the principal product is *tricamphorylstibine chloride*, $(C_{10}H_{15}O)_3SbCl_2$, a substance which, although stable in the presence of mineral acids, is readily hydrolysed by aqueous alkalis, and even by moist silver oxide, into hydrochloric and antimonic acids and camphor. This product is, therefore, much less stable than triphenylstibine chloride, which under similar conditions yields triphenylantimonic oxide.

When triphenylstibine chloride is warmed with alcoholic silver nitrate, it loses both its chlorine atoms, and gives rise to triphenylstibine nitrate, which is partly hydrolysed by hot water to *triphenylstibine hydroxynitrate*, $(C_6H_5)_3Sb(OH)\cdot NO_3$, this product crystallising unchanged from boiling aqueous solutions and also from benzene.

Triphenylstibine hydroxysulphate, $(C_6H_5)_3Sb(OH)\cdot SO_4\cdot Sb(C_6H_5)_3\cdot OH$, is similarly obtained by adding triphenylstibine chloride dissolved in alcohol to a hot aqueous solution of silver sulphate.

***287. "The constituents of Rumex Ecklonianus." By Frank Tutin and Hubert William Bentley Clewer.**

Rumex Ecklonianus, Meisner, is an herb indigenous to South Africa, where it is reputed to possess medicinal properties. An alcoholic extract of this plant yielded, together with resinous products and a small amount of essential oil, the following compounds: Ceryl alcohol; a phytosterol, $C_{30}H_{54}O$, apparently identical with rhamnol; palmitic, stearic, oleic, linolic, and *iso*linolenic acids; a small amount of ipuranol, $C_{25}H_{38}O_2(OH)_2$; kaempferol; chrysophanic acid; emodin;

and emodin monomethyl ether; together with traces of other crystalline substances and large amounts of inorganic salts. A sugar which yielded *d*-phenylglucosazone was also present in small amount, but no evidence could be obtained of the presence of a glucoside. The emodin monomethyl ether which was isolated was identical with that obtained by Perkin and Hummel from *Ventilago madraspatana* (*Trans.*, 1894, **65**, 932), and with that prepared synthetically by Jowett and Potter (*Trans.*, 1903, **77**, 1330). The *dimethyl ether* of *chrysophanic acid* was prepared, and obtained in yellow prisms, melting at 190°.

***288. "The influence of non-electrolytes on the solubility of carbon dioxide in water." By Francis Lawry Usher.**

The solubility of carbon dioxide in solutions of the following substances was measured at 20°: sucrose, mannite, dextrose, glycine, pyrogallol, thiocarbamide, antipyrine, carbamide, acetic acid, catechol, urethane, *n*-propyl alcohol, acetamide, quinol, and resorcinol. The solutions were all *N*/2, with the exception of sucrose, which was examined at four different concentrations. It was found that the change in the solubility of carbon dioxide produced is a linear function of the quantity of sucrose present, for solutions more dilute than *N*/2, on the volume-normal basis of calculation. Of the fifteen substances enumerated above, the first twelve depress the solubility of carbon dioxide, the magnitude of the effect decreasing in the order given, from 26 per cent. in the case of sucrose to 1 per cent. in that of *n*-propyl alcohol. Acetamide, quinol, and resorcinol produce a slight elevation of solubility.

The results were discussed from the standpoint of the theory recently advanced by Philip (*Trans.*, 1907, **91**, 711), which is found to be inadequate to account for the majority of the observations. Jahn's formula, $C_1/C_2 = 1$, was also shown to be inapplicable to the data hitherto available.

It is suggested, in common with Rothmund and others, that the phenomena observed can at present only be referred to mutual interaction of the molecules.

Discussion.

Dr. Philip said that when he presented to the Society his communication dealing with this matter, he had expressed the view that too little attention had been paid to the influence of non-electrolytes on the solubility of gases. Experiments were now in progress bearing on this point.

One important piece of evidence in favour of the hydration theory with which the author had not dealt was the fact that in the great majority of cases $\frac{a-a'}{N}$ increases with dilution, a and a' being the absorption coefficients of the gas in water and solution respectively, and N being the number of gram-equivalents of the dissolved substance per litre. This fact showed that the cause responsible for the lowering of the solubility of a gas was most potent in dilute solution.

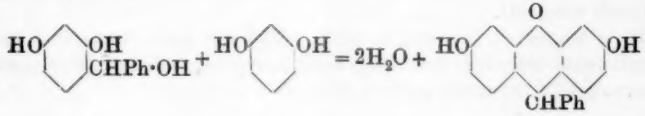
The assumption made in his (Dr. Philip's) paper (*loc. cit.*), that the dissolved substance takes no part in the absorption of gas, should not be indefinitely extended. Obviously, there were many cases, for instance, the aqueous solution of acetic acid used by Mr. Usher, in which the dissolved substance had considerable solvent power for the gas.

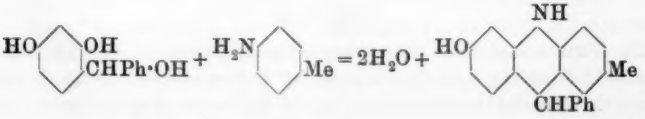
Mr. Usher replied that, as was expected, the equivalent depression of solubility was found to increase with dilution.

The strongest argument against any explanation depending on the assumption that neither the dissolved substance nor the water which might be combined with it had no solvent action was, in his opinion, the observation that, with the majority of the substances examined, the solubility of carbon dioxide in the water of the solutions was in excess of its normal solubility in pure water.

***289. "The condensation of benzaldehyde with resorcinol." By Frank George Pope and Hubert Howard.**

Benzaldehyde and resorcinol in the presence of aqueous solutions of the alkali hydroxides condense to form 2 : 4-dihydroxybenzhydrol. The latter compound also condenses with phenols and with amines in the presence of zinc chloride to yield substituted xanthenes and hydroacridines, thus :





290. "Ethyl α-hydroxy*iso*butyrate." By William Parry.

Ethyl α-hydroxy*iso*butyrate may be conveniently prepared from pure acetone by converting the latter into its cyanohydrin, hydrolysing this, and isolating the resulting acid in the form of its zinc salt.

Anhydrous zinc α-hydroxy*iso*butyrate (100 grams) is then mixed with alcohol (200 c.c.) and sulphuric acid (35 c.c.), and heated on the water-bath for eight hours. After addition of water and extraction with ether, the solution is washed, dried, and the ether distilled. Fractionation of the residual liquid gives ethyl α-hydroxy*iso*butyrate, boiling at 145—150°. After distillation over phosphoric oxide, it boils at 148—150°, and the yield is about half the weight of acetone employed.

The author is studying the action of Grignard's reagents on this ester and on others of similar type.

291. "The action of hydrogen dioxide on thiocarbamides." By Edward de Barry Barnett.

The action of hydrogen dioxide on thiocarbamide and some of its derivatives in neutral and alkaline solution has been studied, and evidence was brought forward to show that under these conditions sulphinic acids are formed.

292. "Chlorination and bromination of acylanilides. Part II. The action of the halogen acids on chloro- and bromo-acylaminobenzenes." (Preliminary note.) By Kennedy Joseph Previté Orton and William Jacob Jones.

In glacial acetic acid solution, hydrobromic acid and acylchloroaminobenzenes and hydrochloric acid and acylbromoaminobenzenes react quantitatively, yielding identical solutions: $Ar{\cdot}NClAc + HBr = Ar{\cdot}NHAc + BrCl$ and $Ar{\cdot}NBrAc + HCl = Ar{\cdot}NHAc + BrCl$ (*Brit. Assoc. Reports*, Winnipeg, 1909). These solutions have been shown tintometrically and by aspiration (compare Orton and Jones, *Trans.*, 1909, **95**, 1456) to contain bromine chloride, which has been found to exist nearly free from bromine and chlorine in this and other anhydrous solvents at 16°. In mixtures prepared by each of these ways, or from the anilide and bromine chloride, a rapid bromination of the anilide occurs, the speed of the reactions being the same in each case. In dilute acetic acids analogous reactions take place, but now

differences appear, and complications are caused by the hydrolysis of the bromine chloride.

Hydrobromic acid and an acylbromoamine react thus: $Ar{\cdot}NBrAc + HBr = Ar{\cdot}NHAc + Br_2$. The interaction has been shown by a tintometric method to be quantitative for glacial and dilute acetic acids. The mixtures are identical (except for the presence of hydrochloric acid) with those prepared from equivalent quantities of the corresponding chloroamine and two equivalents of hydrobromic acid: $Ar{\cdot}NClAc + 2HBr = Ar{\cdot}NHAc + Br_2 + HCl$. Moreover, the speed of bromination in these two mixtures is the same, and also equal to the speed of bromination in the system prepared from anilide and bromine. The velocity of bromination is now, however, very much smaller than in the systems above described, where bromine chloride is present.

If an equilibrium exists between hydrobromic acid, the bromoamine, anilide and bromine in acetic acid solution analogous to that found by the authors (*loc. cit.*) to exist between the chloroamine and hydrochloric acid, the bromoamine and hydrobromic acid are at very small concentration. In such solvents as chloroform and carbon tetrachloride, chloroamines and bromoamines cannot be shown to exist in detectable quantities in the presence of hydrogen chloride and bromide.

The interaction of hydriodic acid and chloroamines in acetic acid solution has been investigated by a tintometric comparison with standard solutions of iodine chloride and iodine. When one molecular proportion of hydriodic acid is used, the reaction is quantitatively $Ar{\cdot}NClAc + HI = ICl + Ar{\cdot}NHAc$; and with two molecular proportions of hydriodic acid: $Ar{\cdot}NClAc + 2HI = Ar{\cdot}NHAc + I_2 + HCl$. Although in aqueous solution, iodine chloride is hydrolysed, the resulting hypoiodous acid then rapidly decomposing in the usual way, it possesses, even in 25 per cent. acetic acid, considerable stability.

These results are in accord with the view suggested recently as to the process of conversion of chloro- or bromo-amines into the isomeric chloro- or bromo-acylanilides (Orton and Jones, this vol., p. 233), namely, that primarily the former react with the halogen acids to form anilide and halogen, which can then interact, producing the *C*-halogen derivative.

293. "A contribution to the study of the oxydases."
By Ross Aiken Gortner.

The author has obtained a new variety of the tyrosine oxidising ferment, tyrosinase, obtained from the larva of *Tenebro molitor*. This variety is distinguished from the known tyrosinases by its insolubility

in water, by its loss of vitality when treated with glycerol, or when subjected to drying, and by its inability to oxidise resorcinol, orcinol, quinol, or pyramidone.

A chromogen has been isolated from the body contents of the larva of *Tenebro molitor*, which gives with tyrosinase, colour reactions identical with those given by tyrosine.

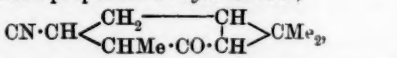
Tyrosinase has also been identified in two examples of myripods, *Scalopocryptops sexpinosa* and *Julius canadensis* (Newp.), in the larva of *Cucujus clavipes*, in the colourless plant, *Monotropa uniflora*, and an observation has been made that extracts of almost all animal tissues possess the power of oxidising quinol.

294. "Experiments on substituted allenecarboxylic acids. Part I." By Arthur Lapworth and Elkan Wechsler.

The authors have synthesised *αγ-diphenyl-γ-1-naphthylallene-α-carboxylic acid*, $C_{10}H_7\cdot CPh{:}C{:}CPh\cdot CO_2H$. It gives a very stable, crystalline compound with ether, but its salts with active bases do not crystallise. The authors have not been successful in resolving the substance into its optically active constituents by any of the ordinary methods.

295. "Cyanocarone." By Reginald William Lane Clarke and Arthur Lapworth.

The preparation and properties of *cyanocarone*,



and some of its derivatives were described. The cyano-ketone very readily gives up the elements of hydrogen cyanide, and is then at once converted into eucarvone. This confirms the usual view of the mechanism of the conversion of carvone into eucarvone, and indicates that the relative stabilities of carbon rings of different sizes may be inverted when a double linking is introduced.

296. "The influence of water on the availability of hydrogen chloride in alcoholic solution." By Arthur Lapworth and James Riddick Partington.

The influence of water on the availability of very dilute solutions of hydrogen chloride in absolute alcohol has been carefully examined. Several tintometric experiments were made with five different specimens of alcohol dried over excess of calcium, two different indicators being employed in all cases but one, involving a large variation in the

total concentration of the hydrogen chloride used. In each case, too, the change in the velocity of esterification of phenylacetic acid by the alcoholic hydrogen chloride, brought about by the addition of water, was estimated. The results prove that within the limits of experimental error, the availability of hydrogen chloride in very dilute alcoholic solution is proportional to concentration of HCl/r + concentration of water, r being identical with the constant used by Goldschmidt and Udby, and termed by them the "hydrolytic constant" of ethyl alcohol hydrochloride, but which the present authors prefer to call the "water-value" of the alcohol. The value of r found was nearly 0·10 at 25° in all cases (that is, 1 litre of alcohol at 25° is equivalent to 0·10 gram-molecule of water), the discrepancy between this and the number 0·15 adopted by Goldschmidt and Udby being apparently due, in the main, to the fact that in the former instance the hydrogen chloride was highly dilute and more fully ionised.

The velocity of esterification of a carboxylic acid in a large quantity of alcohol containing varying small quantities of water is proportional to *concentration of carboxylic acid* × *availability of the catalyst*, and the curve only departs from the unimolecular type in so far as the water formed disturbs the availability of the catalyst.

As the availability of an acid varies enormously with the solvent, even where its concentration and degree of dissociation are similar, the determination of the exact value of this quantity is of primary importance in all investigations connected with salt formation and catalysis in which acids take part.

297. "Amides and imides of camphoric acid." (Preliminary note.)
By William Ord Wootton.

In view of the recent publication of a paper by Abati and Notaris (*Gazzetta*, 1909, **39**, ii, 219), the author stated that he had been engaged for some time past in the examination of a number of derivatives of α-camphoramic acid of the type $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NHR$, together with the corresponding imides. Amongst the substances prepared are the acids and imides arising from the condensation of camphoric anhydride with ethylamine, *n*-propylamine, *n*-butylamine, *n*-amylamine, *n*-hexylamine, allylamine, *o*-, *m*-, and *p*-toluidine, *o*-, *m*-, and *p*-chloroaniline, *o*- and *m*-bromoaniline, *m*-nitroaniline, *p*-aminophenol, *p*-phenetidine, α- and β-naphthylamine.

In the majority of cases the conversion of the acid into the imide, a process involving ring-formation, is marked by considerable diminution in the specific rotation of the compound.

298. **"The nomenclature of imino-compounds and of those compounds exhibiting imino-amino-isomerism." By Jocelyn Field Thorpe.**

Some confusion exists owing to the present system of nomenclature adopted for the imino-compounds.

These substances, which possess the group C:NH, are obviously just as different from the secondary amines having the group $\begin{matrix}C\\C\end{matrix}\!>\!NH$ as the ketones with the group C:O are different from the ethers with the group $\begin{matrix}C\\C\end{matrix}\!>\!O$, yet the general name of imine is applied to both these classes.

It is suggested that as the compounds containing the group C:NH are in many respects analogous to the ketones, the general name *ketimine* should be applied to them, leaving the name imine to be applied to the secondary amines, thus:

C:O	C:NH	$\begin{matrix}C\\C\end{matrix}\!>\!NH$
Ketone.	Ketimine.	Imine.

Moreover, the well-established existence of tautomerism and desmotropism between compounds of the type:

$$CH{\cdot}C(:NH){\cdot}C \quad \text{and} \quad C{:}C(NH_2){\cdot}C$$

renders it advisable to apply some general term to this form of isomerism, similar to the phrase *keto-enolic* isomerism in use with the oxygen derivatives.

It is proposed that the name *ketimine-enamic* isomerism should be applied to this phenomenon.

It is not proposed to alter the name of the *enamic* individual, since such substances can evidently be classified as amino-compounds without entailing any confusion.

Thus, in a compound showing *ketimine-enamic* isomerism, the two forms would be:

$CH_3{\cdot}C(:NH){\cdot}CH(CN){\cdot}CO_2Et$	$CH_3{\cdot}C(NH_2){:}C(CN){\cdot}CO_2Et$
Ethyl β-ketimino-α-cyanobutyrate (*ketimine* form).	Ethyl β-amino-α-cyanocrotonate (ename form).

corresponding with

$CH_3{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et$	$CH_3{\cdot}C(OH){:}C(CN){\cdot}CO_2Et$
Ethyl β-keto-α-cyanobutyrate (keto-form).	Ethyl β-hydroxy-α-cyanocrotonate (enol form).

This nomenclature would be applicable to a number of other classes of compounds in which tautomerism of this kind has been shown to exist, such as the acid amides, the complex ureides, etc.

299. "Dicamphorylphosphinic acid." By Gilbert T. Morgan and W. R. Moore.

Dicamphorylphosphinic acid, $(C_{10}H_{15}O)_2PO{\cdot}OH$, has been obtained by condensing sodium camphor and phosphorus trichloride, and extracting the product with aqueous alkali hydroxides. The study of this compound is in progress.

300. "The combustion of naphthalene and other organic substances, and the atomic weight of carbon." By Alexander Scott.

Although Dumas and Stas (*Ann. Chim. Phys.*, 1841, [iii], **1**, 40) used the combustion of naphthalene, cinnamic and benzoic acids, and some other organic substances to justify their new value of C = 12·00 in preference to that of 12·24, advocated by Berzelius, neither they nor anyone else seem to have recognised or utilised the advantages of such a substance as naphthalene for affording data for an accurate determination of the atomic weight of carbon.

The experiments of Dixon, Baker, and others suggest that it is more than likely that the combustion of pure *dry* carbon in *dry* oxygen might lead to carbon monoxide escaping even with a large excess of oxygen. The combustion of a hydrocarbon would lessen any loss from such a cause enormously, as some trace at least of water may be assumed to be present throughout the combustion. Each gram of naphthalene burnt ought to give 3·4359 grams of carbon dioxide if C = 12·000 and H = 1·0075, but if C = 12·018 only 3·4325 ought to be produced, hence for a difference of 0·018 in the atomic weight of carbon we get a difference of 3·4 milligrams in the carbon dioxide produced.

Two series of combustions have been carried out with naphthalene, one set in a glass tube and the other in a quartz tube, both in a current of oxygen. In all, six experiments were made, and 17·6175 grams of naphthalene gave 60·5355 grams of carbon dioxide, hence 1 gram of naphthalene gave 3·4361 grams of carbon dioxide, whence C = 11·999.

Similarly, with cinnamic acid each gram ought to yield 2·67459 grams of carbon dioxide if C = 12·000, but only 2·67276 if C = 12·018. Two experiments have been made, giving together 8·61537 grams of cinnamic acid, which yielded 23·0413 grams of carbon dioxide, that is, 1 gram of cinnamic acid yielded 2·67444 grams of carbon dioxide, whence C = 12·0015.

These results therefore agree with all other combustion and physical results in indicating that C = 12·00. The cause of the discrepancy

between these results and those derived from the alkylammonium bromides remains still to be discovered.

It might be thought that the enormous number of combustions of organic compounds which are continually being made would have indicated whether C = 12·000 or C = 12·018 were the correct number. This is hardly likely, however, for if we calculate the percentage of carbon in naphthalene, taking C = 12·00 and C = 12·018, this comes out 93·706 and 93·715 respectively, and both would be stated as 93·71 per cent. within the limits of experimental error.

The weights given above are all corrected to vacuum standard.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Allen, *Alfred Henry.* Commercial organic analysis. A treatise on the properties, modes of assaying, and proximate analytical examination of the various organic chemicals and products employed in the arts, manufactures, medicine, etc. With concise methods for the detection and estimation of their impurities, adulterations, and products of decomposition. 4th edition. Edited by *Henry* **Leffmann** and *W. A.* **Davis.** Vol. I. pp. x + 576. ill. London 1909. (*Recd.* 9/12/09.) From the Publishers: Messrs. J. & A. Churchill.

Crookes, *Sir William.* Diamonds. pp. xvi + 146. ill. London 1909. (*Recd.* 13/12/09.)

From the Publishers: Messrs. Harper & Brothers.

Eijkman, *J. F.* Tafeln zum gebrauche bei der Bestimmung von Brechungsindices nach der Methode der konstanten Deviation von 40°. pp. [102]. Groningen 1909. (*Recd.* 10/12/09.)

From the Author.

Gemmell, *George Harrison.* Chemical notes and equations, inorganic and organic. 2nd edition. pp. xiii + 265. London 1909. (*Recd.* 10/12/09.)

From the Publishers: Messrs. Baillière, Tindall, and Cox.

Morgan, *J. Livingston R.* Physical chemistry for electrical engineers. 2nd edition. pp. x + 249. New York 1909. (*Recd.* 10/12/09.) From the Publishers: Messrs. John Wiley & Sons.

Thorpe, *Sir Edward.* History of chemistry. Vol. I. From the earliest times to the middle of the nineteenth century. pp. viii + 148. ill. London 1909. (*Recd.* 10/12/09.)

From the Publishers: Messrs. Watts & Co.

Van Nostrand's Chemical annual, 1909. A hand-book of useful data. Edited by *John C.* **Olsen.** pp. xii + 580. London 1909. (*Recd.* 10/12/09.)

From the Publishers: Messrs. Constable and Company.

II. *By Purchase.*

König, *Franz Josef.* Chemie der menschlichen Nahrungs- und Genussmittel. 4th edition. Vol. III. Untersuchung von Nahrungs-, Genussmitteln und Gebrauchsgegenständen. Teil I. Allgemeine Untersuchungsverfahren. pp. xiv + 772. ill. Berlin [1909]. (*Recd.* 7/12/09.)

Lunge, *George.* The manufacture of sulphuric acid and alkali, with the collateral branches. 3rd edition. Vol. II. Sulphate of soda, hydrochloric acid, Leblanc soda. 2 vols. pp. xx + 490, xii + 493 to 1010. ill. London 1909. (*Recd.* 4/12/09.)

JULIUS THOMSEN MEMORIAL LECTURE.

The Julius Thomsen Memorial Lecture will be delivered by Professor Sir Edward Thorpe, C.B., F.R.S., at the Ordinary Scientific Meeting on Thursday, February 17th, 1910, at 8.30 p.m.

PRESENTATION TO PROFESSOR KOERNER.

A Committee has been formed in Milan with the object of celebrating the seventieth birthday of Professor Koerner. It is proposed to devote subscriptions to the following purposes:

1. Foundation of a prize for work in pure and applied chemistry.
2. Reprinting Professor Koerner's works.
3. Presentation of a gold medal to Professor Koerner.

The Treasurer of the Chemical Society will be glad to receive subscriptions, and will forward them to the Organising Committee.

TABLES OF INTERNATIONAL ATOMIC WEIGHTS, 1910.

To encourage the use by Students of the Tables of Atomic Weights, as issued by the International Committee, the Council has decided to offer the Tables at the following prices:

On **Cards**: 1/- per doz.; 4/- per 50; 7/6 per 100.
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(Note: The Tables printed on paper are suitable for pasting into note-books.)

At the next Ordinary Scientific Meeting on **Thursday, January 20th, 1910, at 8.30 p.m.**, the following papers will be communicated:

"The alkaloids of ergot. Part II." By G. Barger and A. J. Ewins.

"The constituents of colocynth." By F. B. Power and C. W. Moore.

"The triazo-group. Part XI. Substituted triazomalonic and phenyltriazoacetic acids." By M. O. Forster and R. Müller.

"Iodobenzenemonosulphonic acids. Part II. Esters and salts of di- and tri-iodobenzenesulphonic acids." By Miss M. Boyle.

"Organic derivatives of silicon. Part XII. Dibenzylethylpropylsilicane and sulphonic acids derived from it." By F. Challenger and F. S. Kipping.

"The absorption spectra of naphthalene and of tetramethylnaphthalene." By Miss A. Homer and J. E. Purvis.

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